

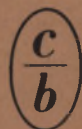
LTMRAR 12(6) 617-752 (1977)

LITHOLOGY AND MINERAL RESOURCES

ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ

(LITOLOGIYA I POLEZNYE ISKOPAEMYE)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

LITHOLOGY AND MINERAL RESOURCES

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Subscription
(6 Issues): \$250

Single Issue: \$50
Single Article: \$7.50

Prices somewhat higher outside the United States.

CONSULTANTS BUREAU, NEW YORK AND LONDON



227 West 17th Street
New York, New York 10011

Published bimonthly, consisting of Volume 12 issues 3 through 6 and Volume 13 issues 1 and 2. Subscription price for Volume 12 is \$225, and for Volume 13 is \$250. Second-class postage paid at Jamaica, New York 11431.

Lithology and Mineral Resources is abstracted or indexed in *Engineering Index*.

LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

July, 1978

Volume 12, Number 6

November-December, 1977

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The Russian press date (podpisano k pečati) of this issue was 1/28/1977.
Publication therefore did not occur prior to this date, but must be assumed
to have taken place reasonably soon thereafter.

Calculation of absolute volumes of terrigenous and biogenous material in the oceans shows that, contrary to data of balance calculations, biogenous material of the pelagic zone is roughly half of total sediments. About 92% of terrigenous material is deposited along the oceanic periphery, this being mainly the river load. It is demonstrated that two other mechanisms of processing and transportation of terrigenous material — aeolian and glacial — are not inferior in importance to the fluvial, and are the critical ones in areas of their principal development. It also is demonstrated that the geochemical process in the ocean is not a "process of mechanical scattering and fractionation of solid phases that have come from the coast," as believed by N. M. Strakhov. The scale of biogenous process in the oceans is much greater than that of terrigenous sedimentation. All of the sedimentary material from the coast (in solution and in suspension) repeatedly passes through alimentary systems of organisms and is assimilated and filtered by them.

In our preceding article (Lisitsin, 1977), we have demonstrated the zonal character of oceanic sedimentation. Depending on climate, the biogenous process may be extremely weak (glacial zones) to weak with mainly the carbonate deposits laid down (arid zones), to intensive when carbonate sedimentation is augmented by voluminous silica accumulation (humid zones). Both the terrigenous and biogenous sedimentations proceed in three stages: processing, transportation, and accumulation. All these stages exhibit clean-cut features of their own, depending on climate. The zones are set up in the ocean, where the organisms assimilate the dissolved salts and produce suspension material differing from zone to zone in composition and properties (carbonates, opal silica, chitin, organic substances, etc.). The groups of organisms (bio- and thanatocenoses) responsible for the sedimentary material are always associated with definite climatic zones. Consequently, the ocean floor in the pelagic zone accumulate biogenous deposits differing in position (determined only by climatic zones), properties, and composition. The bulk of sedimentary material in pelagic zones is developed independently of land, out in the open sea; and the very origin of the biogenous process is controlled by the environment.

All of the terrigenous material originates on the continents and arrives to the pelagic zone from regions of different climate. The question is, whether the composition and properties peculiar to this material are preserved, or is there a mixing of material from different sources, so that the terrigenous material of the pelagic zone is an averaged-out sample of the continental material? Also, what is the relationship between terrigenous and biogenous material in the oceans?

Actual Role of Terrigenous Material in Oceanic Sedimentation

The current view in the field of lithology and geochemistry of the oceans has it that terrigenous material is greatly predominant over the biogenous. This view is supported by balance calculations, including my own (Lisitsin, 1974), cited in the most recent publication of N. M. Strakhov (1976). According to these calculations, the total annual inflow of terrigenous material into the oceans is 22.1 billion tons: river load, 18.53 billion tons; glacial discharge, 1.5 billion tons; aeolian transfer, 1.6 billion tons; and coastal abrasion about 0.5 billion tons. By correlating these figures with inflow of biogenous material, likewise determined from discharge of the corresponding elements from land (car-

bonates, 1.36 billion tons; silica, 0.46 billion tons; a total of 1.82 billion tons, i.e., 7.6% of total volume), Strakhov concludes that "These calculations radically modify the conventional views on the character of oceanic geochemical process. If the latter is understood to consist of concrete phenomena and processes responsible for the chemical composition of sediments, the implication is the oceanic geochemical process is 90-93% physical, more precisely mechanical, i.e., a process of mechanical scattering and fractioning of solid phases, allochthonous, coming in from the coast. This physical process is only 6.0-9.2% complicated by the biogenous..." (Strakhov, 1976₂, p. 201; italics ours, A. L.)

Furthermore according to Strakhov, distribution of this allochthonous material over the oceans is hydrodynamically controlled, with the zones of circular currents marked by higher absolute volumes of the elements and their low percentage. To quote Strakhov, "The only correct general interpretation of geochemical process in the oceans is, in the author's opinion, the hydrodynamic concept developed in the preceding pages. It is consistent with so many facts that one wonders at its absence in the literature. The reason probably is that oceanic lithologists dealt only with concrete points of the history of the several components in the one ocean or another without tying them together. In addition, they operated only with percentages. The advent of data bearing on the rate of oceanic sedimentation in total and with reference to its components, and also on absolute volumes, immediately moved the subject to a new and more general plane" (Strakhov, 1976₂, p. 203). However, in recent years, independent methods have yielded facts modifying the concept of predominance of river suspension in the pelagic oceanic sedimentation. There are at least five groups of such facts.

1. Direct study of the ratio of suspension and solution forms of the elements in ocean waters, and their comparison with forms typical of river waters. The average values obtained for the oceans show that solution rather than suspension is the principal form of existence for the majority in the oceanic pelagic zone (Lisitsin and Gordeev, 1974).

2. Direct determination of the contribution of codeposited elements and those sorbed from water, including their portion bound with solid suspension (correlation of reactive forms of the elements and the clastic forms), in sediments. The extant data on many elements in pelagic sediments indicate that a considerable (usually predominant) portion of elements is not bound either with the clastic fraction of the mechanical dispersion of solid phases but is instead the result of sorption and coprecipitation, i.e., they are captured from solution in ocean water.

3. Data on mean composition of oceanic waters. A store of several thousands of representative points for analyses of sediments would characterize the mean composition of sedimentary material in the pelagic zone. Up to recently, a mere 100-150 complete silicate analyses of oceanic sediments have been published, an amount inadequate for such calculations. The Oceanology Institute has come into possession of mass material bearing on composition of surface sediments and also drillhole cuttings for the World Ocean: a total of 3500 complete silicate analyses. According to these data, the mean content of CaCO_3 in pelagic sediments is 34% for the present sediments and even higher (43%) in drillhole cuttings, up to 150 million years old, an average of 36.2%. The corresponding figures for amorphous SiO_2 are 4.60% for the present sediments and 2.4% for drilling samples (all figures reduced to natural dry sediments); for the entire oceanic sedimentary sequence, this is an average of 4.20%. Thus, biogenous material for the sedimentary oceanic sequence, $\text{CaCO}_3 + \text{SiO}_2\text{-amorph} + 2 \times \text{C}_{\text{org}} = 36.2 + 4.20 + 2 \times 0.24 = 40.9\%$, i.e., the mean ratio of terrigenous and biogenous material in sediments is markedly different from the one obtained by Strakhov.*

4. Another independent method is based on calculation of bottom areas occupied by present sediments of various types. In first approximation, areas of the biogenous and the

*Opal of marine plankton contains an average of 10-15% water. Consequently, the true content of opal is higher than of $\text{SiO}_2\text{-amorph}$, as chemically determined. The chemical method (repeated soda extraction) yields systematically lower figures as compared with IR spectroscopy: by a factor of 2.7 for contents lower than 10%, and by a factor of 1.25 for contents over 50% (Levitan, 1975). In addition, opal of radiolarias passes only partially into soda extracts. As a result, the largely chemically obtained data bearing on opal content in bottom sediments should be considered as minimal. The more accurate values may be higher by a factor of 1.5-2.0.

TABLE 1. Absolute Volumes of Terrigenous and Biogenous (carbonate and siliceous) Material in River Load and in Pelagic Oceanic Sediments (numerator, billion tons a year; denominator, % content)

Sedimentary material	River load	Pelagic oceanic sediments			
		Atlantic	Indian	Pacific	World Ocean
Terrigenous	22,1	0,642	0,304	0,784	1,730
	92,4	52,19	50,88	67,90	58,02
Biogenous	1,82	0,588	0,293	0,37	1,251
	7,6	47,8	49,11	32,08	41,98
carbonate (CaCO ₃)	1,36	0,543	0,231	0,305	1,079
	5,7	44,14	38,74	28,48	38,22
siliceous (SiO ₂ -amorph)	0,46	0,045	0,069	0,065	0,172
	1,9	3,66	10,37	5,62	5,76
Total:	23,92	1,230	0,597	1,154	2,981
	100	99,99	99,99	99,98	100

terrigenous sediments reflect the ratios of these kinds of material in the ocean. The author, in cooperation with V. N. Lukashin, has calculated these areas from the map of types of sediments in the World Ocean, compiled at the Oceanology Institute in 1976. The sum of areas of the biogenous sediments (with over 50% CaCO₃ + SiO₂-amorph) is 39.15% of the total area of pelagic sediments, a figure very close to that cited above for the mean content of oceanic sediments.

5. The most convincing data militating against Strakhov's concept of the character of oceanic sedimentation and the place of terrigenous material in it are obtained from direct calculations of absolute volumes of that material as compared with the calculated absolute volumes of biogenous material. It should be noted that reliable calculations of absolute volumes of sedimentary material have become feasible in principle only after publication of the first maps of sedimentation rates for the several oceans and then for the World Ocean as a whole (Lisitsin, 1974). It took about 15 years to develop the methods and principles of compiling such maps.

As a result, the first maps were drawn for absolute volumes of sedimentary material for the several oceans and the World Ocean as a whole (Lisitsin, 1974) and then the maps of sedimentary components: terrigenous, biogenous, individual elements, mineral, and fractions (Lisitsin, 1977, 1, 2). On the basis of these maps, we have succeeded in determining for the first time by direct method (rather than from the balance of discharge) the amounts of biogenous and terrigenous materials annually deposited in the pelagic zone of the ocean. The results of these calculations are listed in Table 1. They characterize the ocean floor, mainly regions with depths of over 3000 m and accounting for over three-fourths of the World Ocean area. These calculations show that only 1729 billion tons or 7.8% of the 22.1 billion tons of total terrigenous material coming from the continent, reaches the pelagic zone, while the bulk of this material (92.2%) is dumped along the oceanic periphery (near river mouths, in marginal seas, in trenches, and at the base of the continental slope). As such, they do not participate in pelagic sedimentation. Hence, the true ratio of terrigenous and biogenous material in the pelagic zone turns out to be different than that calculated by Strakhov.

The fact of a preferential deposition of terrigenous suspension in marginal seas, near river mouths, and along the oceanic periphery can be inferred also from the map of sedimentation rates in seas and oceans (Lisitsin, 1974). To cite the most illustrative figures, average rate of pelagic sedimentation (B) in the oceans usually falls within the 1-5 mm/1000 years. This compares with the rate of deposition for terrigenous material near the mouths of the Red and Mecong rivers, 30,000 B; Mississippi, 10,000 B; Orinoco, Kura, and Rhone, (5000-6000) B. These figures are fairly high also for the interior seas with a predominantly terrestrial sedimentation: (300-6000) B for the Caspian Sea; (1000-2500) B for the Sea of Azov. For the marginal seas: Okhotsk, from 25 B to over 500 B; Bering, from 50 B to over 500 B; etc. The rates along the oceanic periphery, at the base of the continental slope, usually are (10-100) B and over.

Because the bulk of terrigenous suspension is deposited offshore, the inflow of dissolved carbonates and silica (accounting for a mere 1.82 million tons, or 7.6% of river load)

to the pelagic zone turns out to equal that of terrigenous material (1.82 billion tons and 1.729 billion tons, respectively). In other words, the average composition of pelagic sediments must correspond in that event roughly to equal contents of the biogenous and terrigenous fractions (roughly 50% biogenous material).

These data, obtained by independent methods, yield an average of at least 40-50% for the content of biogenous material in pelagic oceanic sediments. This figure is fairly consistent from method to method and differs greatly from the 6-9% of biogenous material, according to Strakhov's calculations.

Thus, Strakhov's concepts of the character of sedimentation at the ocean floor are inconsistent with reality. Even more remarkable is the fact that this inconsistency is exposed precisely by the method of absolute volumes' calculations. This conclusion is crucial in understanding the entire course of oceanic sedimentation and makes it possible to do away with many misunderstandings.

Thus, calculations by the method of absolute volumes demonstrate that, by considering both the biogenous material and the sorbed forms of the elements, the bulk of material annually accumulating on the ocean floor is not bound with fractionation of mechanical suspension brought in by rivers. Instead, it originates in the pelagic zone far away from areas of material brought in from land (biogenous material), beyond the zone of differentiation and beyond the region of "circular" currents. The remaining portion is substantially transformed by the living organisms. Consequently, the principal processes determining the geochemistry of oceanic sediments are a mobilization of dissolved substances in the pelagic zone and bringing them into suspension, accompanied by deposition of very fine terrigenous suspension. The scale of these processes is comparable, and their role changes from one oceanic region to another, depending on natural conditions (zonation). At the same time, terrigenous material in the ocean is subject to particularly intensive action of living organisms, discussed below.

Actual Character of Transfer of Terrigenous Material to the Pelagic Zone

According to the balance calculations, river load accounts for about 84% of terrigenous material brought into the ocean, with 6-7% accounted for by the aeolian and glacial material. The total contribution to oceanic sedimentation by the two last-named factors is only about 14%, i.e., ostensibly insignificant. However, as in general balance calculations by the percentage method, an error is introduced which distorts the actual ratios of various terrigenous materials in the pelagic zone. As already noted, over 90% of river load is deposited near the mouth, in the peripheral zone of differentiation. As to the two secondary (in balance calculations) types of terrigenous material (glacial and aeolian), they bypass without a substantial loss the peripheral zone of deposition for river material.

The moraine material is transported by icebergs over the oceanic surface and is dropped where the ice begins to melt, i.e., where climatic conditions induce melting.

The aeolian material reaches the pelagic zone at distances of 5000-6000 km from land, largely at upper levels of the troposphere and in the stratosphere, with the locally blown material deposited at the periphery of the ocean. Distribution of both the aeolian and glacial material does not depend on the circular currents. It is controlled by air dryness that ensures a maximum capture of land material and its long distance transfer over the ocean; and also by wind pattern. In highly humid air, aerosols are rapidly flushed out by atmospheric precipitation. All in all, aeolian transportation is controlled by climatic factors also.

A comparison of contribution by the glacial (1.5 billion tons) and aeolian (about 1.6 billion tons) material with total volume of terrigenous material deposited in the pelagic zone, as determined from the absolute volumes (1.73 billion tons a year), clearly shows that the role of glacial and aeolian material in pelagic sedimentation is not inferior to that of river load; and that the view of their secondary importance is based on an erroneous, in our opinion, method of calculation.

Interaction of the Terrigenous and Biogenous Sedimentation Processes in the Ocean

The figures cited fall far short of completely characterizing the actual scope of biogenous processes in the pelagic zone — because the carbonate, siliceous, and chitinous tests and the cellular plasma (C_{org}) constitute only an insignificant fraction of biogenous material annually lost from the biogenic cycle. The following figures illustrate the true scope of this global process. Some 110 billion tons of dry plankton substance are produced annually at the ocean surface in a mobilization of dissolved salts (Bogorov, 1971), or 4 times the total discharge from land and inflow of volcanic material to the ocean. However, a comparison of total biogenous material with that of terrigenous and volcanic actually reaching the pelagic zone (1.73 billion tons) shows a huge preponderance of biogenous material over the terrigenous in the pelagic zone — by a factor of 50-60. According to my calculations by the method of absolute volumes, a mere 1.251 billion tons of biogenous material (carbonate and siliceous tests) annually originating in dissolved forms on the ocean surface reach the ocean floor (Table 1). By adding to that the roughly 0.06 billion tons of C_{org} buried annually in the ocean floor (Romankevich, 1975), we obtain about 1.3 billion tons, or a mere 1.2-2.0% of dry plankton substance, less by a factor of 50-70 than produced at the surface. In other words, biogenous oceanic sediments only hint at the huge scope of biogenous process whose full force is manifested at the stage of preparation and transportation of sedimentary material.

The average figure obtained in direct calculation of absolute volumes is of the same order as the one earlier determined for various components of suspension load and bottom sediments, from the degree of preservation of various biogenous components in pelagic sediments: SiO_2 -amorph, 0.4-2.0% (locally 10%); C_{org} , 2-5% (Lisitsin, 1954; Bogdanov et al., 1971; Romankevich, 1975). The biogenous process is of most importance at the preparation and transportation stages for sedimentary material, including the terrigenous. Lithologically the most important processes associated with marine organisms are as follows.

Bioassimilation, transfer of water-dissolved salts to solid substance of tests and the organic plasma compounds. This process takes place out in the open ocean and is unrelated to the continents. The tests of bottom organisms account for over 40-50% of total sedimentary material that reaches the pelagic zone (Table 1).

Biofiltration, extraction of detritus out of water by zooplankton and benthos, as nourishment with a simultaneous capturing of terrigenous suspension and processing it to coarse alimentary nodules. This is the principal mechanism of deposition for very fine terrigenous material within the pelagic zone; it ensures a rapid elimination of terrigenous material from surface waters rich in plankton.

Biosorption, enrichment of upper layers of the pelagic zone in considerable amounts of carbonate, siliceous, and chitinous sorbents: finely fragmented phytoplankton tests produced by zooplankton crayfishes; and also in organic sorbent — detritus. These natural sorbents capture many elements dissolved in oceanic water. At the same time, Mn and Fe are of great importance. They are present in the plasma of organisms; following its decay, these elements form fresh colloid hydroxides in waters below the surface layer and also of the upper layer of sediments. These are the most active oceanic coprecipitators and sorbents; they concentrate the minor elements. Thus, the organisms participate in converting the dissolved Fe and Mn into colloid coagulations which then capture the minor elements in coprecipitation and then in sorption. Participation of the organisms in supplying the oxyhydrate sorbents may be designated as bioproduction of collectors which control on the whole the geochemistry of minor elements in the oceans.

Biological transportation comprises transfer of terrigenous and biogenous suspension by filtering organisms (zooplankton) in their considerable vertical migration (diurnal and others), as well as — and to a greater extent — the general transfer of material and energy by detritus (suspension) descending from surface layers of the ocean, the site of photosynthesis, all the way to the bottom.

An important difference between the biogenous and terrigenous material in the ocean is a transitory character of the first: its bulk is not buried in sediments but constitutes the principal factor of material and energy transfer from surface layers to the deeper, all the way to the bottom; it also participates in transformation of the elements and compounds.

The bioassimilation processes lead to a concentration and transformation of water-dissolved elements and compounds into suspension forms: skeletal formations and protoplasm of phytoplankton and zooplankton bacteria; and through their agency — to skeletal formations and tissue of zooplankton, benthonic, and nektonic organisms. Extensive studies of these processes have been carried out by A. P. Vinogradov (Vinogradov, 1953, 1967).

Capability of the organisms to concentrate the needed elements from ocean water is amazing. There are known instances of ten- and hundred thousand-fold concentration with an almost complete extraction of the elements from ocean water. To quote Vinogradov (1967, p. 89), "The live substance in the ocean is endowed with an immense number of geochemical functions. Many of these are known, many more remain to be studied, and there are many waiting to be discovered. Unquestionably, the organisms and their detrital organic substance not only are instrumental in transportation of sediments to the ocean bottom but their role in this sedimentation process is enormous." The scope of this process is illustrated by calculations on the basis of average absolute volumes, with consideration given only to the most common macro-components. Similar calculations have been carried out for many microcomponents.

By dividing the volume of terrigenous material in the pelagic zone (1.73 billion tons a year) by the area of this zone with depths over 3000 m (277 million square km) we obtain a modulus of terrigenous pelagic accumulation, 6.2 g/m^2 a year. At the same time, about 50 g/m^2 of Corg is produced annually at the ocean surface (Romankevich, 1975). Considering that at least 70% of this production is accomplished by diatom algae, the characteristic ratios of the elements (Lisitsin, 1964) can be used in determining the amount of other elements annually bound (produced) by plankton to 1 m^2 of surface: 92 g of SiO_2 -amorph, 15 g Fe, 2 g P, 0.03 g Mn, and 0.06 g TiO_2 , a total of about 160 g. In the southern and main silica-accumulating belt of the World Ocean, the average rates of primary production are much higher, about 90 g/m^2 (correspondingly, 136 g SiO_2 -amorph, 26 g Fe, 3.5 g P; 0.05 g Mn; 0.11 g TiO_2 ; a total of about 263 g). According to Bogorov (1971), an even larger amount of substance is produced annually under 1 m^2 of ocean surface, about 377 g/m^2 : some 195 g of organic matter + 142 g mineral (zonal). To be sure, the estimated figures vary somewhat depending on the method and area of investigation; nonetheless, it is quite obvious that, despite all the discrepancies, the biogenous process of the pelagic zone is, on the whole, tens of times more intense than the terrigenous, with processes of preparation, transportation, and deposition of organic sedimentary material being the predominant.

Terrigenous suspension sinks to depths by gravity, according to the Stokes law, under conditions of mobility of waters at all depths. Actually, the biogenous mechanism of bio-filtration is of telling importance.

The majority of zooplankton organisms are biofilters. They obtain nourishment by passing ocean water through a fine filtering device which retains the phytoplankton and organic detritus. Such filtering organisms are infusoria, tunicata, zooplankton crustaceans (Copepoda, Euphausiatae, Amphipoda), certain fishes, and whales. The filtering organisms are fitted not for a selective use of biogenous suspension, alone. Instead they filter off all the material, including the terrigenous, and bind it up into coarse nodules. In the struggle for suspension food, different associations of filtering organisms, with filtering facilities of their own, are developed in different zones. Used for that purpose are various lattices, paw-mesh, mucous chambers, and other devices. The daily need of filtering organisms for suspension fluctuates from 2 to 10% of their weight; however, excessive consumption also is widespread. For example, the crayfish-copepods, particularly abundant in plankton, may consume as much as 30-40% of their own weight in food.

The scope of filtration process is astounding. The biomass of oceanic zooplankton is 21.5 billion tons (Bogorov, 1971); it consumes about 6% of its weight in food daily, i.e., some billion tons of phytoplankton organisms, detritus, and terrigenous suspension. Inasmuch as suspension in surface layers of the ocean is about 20% organic matter, zooplankton must capture some 5 billion tons of suspension to secure its daily nourishment. In other words, it must eliminate suspension from some $50,000 \text{ km}^3$ of ocean water a day.* Although these calculations are approximate, they indicate the immense scope of a process that goes on inconspicuously in ocean waters, particularly in their upper active layer — a process of immense importance in sedimentation. As determined by the study of suspension, this mecha-

*Annual water discharge of rivers of the world is about $37,000 \text{ km}^3$, i.e., almost 1/500 of water volume annually filtered by plankton alone.

nism clears the surface oceanic waters of their terrigenous biogenous particles. The rate and thoroughness of this operation increase with plankton production.

The efficiency of water purification by filtering organisms fluctuates from 1-5 μ for organisms with a comparatively coarse filtration to 0.3 μ and less for very fine filters. There is a climatic and vertical zonation in the distribution of filtering organisms: namely, the finest ones favoring the surface waters while the coarser inhabit the depths.

Practically none of the terrigenous suspension of the upper layers in the pelagic zone does settle down mechanically, nor it is fractioned, as believed by Strakhov. Instead, it is removed from surface layers by organisms as alimentary particles measuring from tens of microns to 1-4 mm. These particles are recirculated many times by deep plankton and benthonic filtering organisms. A direct study of these particles was made on suspension in membrane filters (Lisitsin, 1961; Lisitsin and Bogdanov, 1970) as well as on material captured by plankton nets, and recently by means of special sedimentation traps installed on the ocean bottom. Sedimentary material from a trap left for 63 days in the Bahamas area, at a depth of 2000 m, consisted solely of cylindrical particles about 240 μ long, 100 μ in diameter (Wiebe et al., 1976). It was possible to determine the absolute volume of particles so deposited: 650 pieces/ m^2 /day. The rate of their depositions fluctuates depending on their size, from 50 to 941 m/day, an average of about 150 m/day, which is close to figures cited by other authors: 36-376 m/day. The average size of original, not lumped together, particles in oceanic suspension is about 1 μ (Lisitsin, 1961); their rate of sinking, a mere 1.5-2.0 m/day. Biofiltration speeds up thousands-fold the deposition of particles and rapidly cleans up the surface waters of fine terrigenous suspension that reaches the pelagic zone. The end result is its rapid elimination from the upper circulation system.

Important changes take place at the bottom. They are related to deposition of lumped particles in places unfavorable for fine material. For example, particles measuring 10 μ are not deposited when the bottom current velocity is over 1 cm/sec. The same particles in lumps of 240 μ can accumulate in areas of 7-cm/sec currents (the usual bottom current velocity is 3-5 cm/sec and over). After a time, organic cement of the lumps decays, and the lump breaks up into its component smaller particles, which leads to a general disturbance in mechanical differentiation. The fine material now gets to areas inaccessible to it because of hydrodynamic conditions. That the actual pelagic sedimentation is far from simply mechanical can be inferred from maps of distribution of pelitic and subcolloid fractions in bottom sediments, as for example in the Pacific Ocean (Sedimentation..., 1970, pp. 300-301). The finest subcolloid particles do not accumulate in central reaches of the ocean (farthest away from the continents) but along the oceanic periphery. This means that the main factor of their distribution is not a simple mechanical fractionation; they concentrate both in the halistatic regions and beyond them, in Antarctica.

Biofiltration is the principal mechanism of removing fine terrigenous and biogenous suspension not only from the surface oceanic waters. It is a potent factor in regions of great benthonic biomasses: over the shelf and in the upper part of the continental slope, i.e., along the path of suspension transfer. As demonstrated in numerous experiments, a large mussel mollusk filters 3-6 liters of water per hour and fully captures particles measuring less than a mm. This property of mollusks is used in purifying aquarium water and basin water. As directly observed, a 1- m^2 column colony of mussel in the Black Sea filters 100-1000 metric tons of water per day, with all the suspension eliminated by combining it in very coarse alimentary lumps. The filtering organisms make up continuous large belts along the paths of suspension inflow and the principal directions of its transportation. They are forced to shift in areas of periodical inflow of suspension, and transfer their filtration facilities to areas of maximum inflow. Here, terrigenous suspension is rapidly removed from surface waters by gravity and the powerful biofiltration mechanism. Its further fate is not related to the surface circulation system, contrary to Strakhov's opinion.

The surface of tests of plankton organisms is very well developed and constitutes an important natural sorbent. Diatomaceous earths are extensively used in industry; the sorbing properties of dead organisms are well known (in concentrations of V, U, and other elements) as are those of fish bones and teeth, and finely fragmented carbonate material. Production of a considerable amount of biosorbents in pelagic reaches of the ocean is an important contribution to the oceanic sorption system as a whole. Other substantial contributions to the sorption balance are inflow of terrigenous sorbents (clay minerals), endogenous sorbents (in regions of metalliferous sediments near the active mid-oceanic ridges), and authige-

nous sorbent minerals and formations (Fe-Mn concretions and microconcretions, glauconite, phillipsite, sulfides, and others).

Concentration of the majority of microelements in oceanic water is so low that the products of dissolution even of the most soluble of their compounds are not assimilated anywhere in the ocean and remain in water as an ultradiluted solution. The principal mechanism of transferring the majority of elements from solution to bottom sediments is the biogenous, including the sorption process by the agency of biosorbents.

The biogenous process is characterized by a lack of stability in the sorbent itself and its disappearance at depths and in the upper layer of sediments. As pointed out before, biogenous transportation, including that by sorption, proceeds on a huge scale, involving among other things, transfer of minor elements to deep layers of the ocean and to bottom sediments. Biogenous transportation is of importance also in development of colloids in oceanic water, by condensation (as opposed to the conventionally considered dispersion). The gist of this operation is exchange of the solvent (plasma of organisms at its decay) for oceanic water. This process is particularly important in development of Fe and Mn oxyhydrates, the most potent oceanic coprecipitants and sorbents.

Years of long investigations by Yu. A. Bogdanov, E. I. Gordeev, and the author have shown that surface waters and oceanic depths carry widespread particles of organisms colored by indicators of Fe and Mn. They disappear in the surface layer, replaced by Fe and Mn hydroxides. Thus, the organisms play the role of "transportation packaging." This packaging is broken up in the upper layer, organic matter is destroyed, and Fe and Mn pass into water to form fresh oxyhydrates. They extract minor elements out of bottom and ooze water by coprecipitation and then by supplementary sorption at the free surface. Similar phenomena take place in dissolution of CaCO_3 and SiO_2 -amorph, of the organisms' tests. The scope of this process can be evaluated. According to the most recent data, annual production of Corg by plankton is roughly 20 billion tons. The average Fe/C ratio for diatom plankton is 0.11 (Lisitsin, 1964). This means 2 billion tons of Fe annually bound up as protoplasm, and subsequently passing into water as colloids (Fe oxyhydrates), a figure close to the total terrigenous material deposited at the bottom of the pelagic zone. The bulk of Fe is again used recurrently by plankton. In this operation, surface waters are gradually cleared of dissolved elements by bringing them into suspension through coprecipitation and sorption by Fe oxyhydrates. The total amount of iron deposited at the ocean bottom cannot exceed its inflow from land and with the endogenous material, but the figures cited indicate the huge scope of this process of mass generation of colloids by organisms — a process which the lithologists have failed to consider up to now.

Thus, the biogenous process in the ocean is not only a powerful assimilation mechanism of bringing into suspension the dissolved forms of elements. It is a chain of interrelated processes of developing colloid condensation on finely dispersed organic matter (Corg, CaCO_3 , SiO_2 -amorph, and others). Distribution of mechanisms of bioassimilation, colloid development, and biosorption is controlled by plankton zonation (latitudinal, vertical, circumcontinental). The field data cited here demonstrate that, under conditions of a "live ocean," sedimentation cannot be considered as a physical — more precisely mechanical — process, i.e., mechanical dispersion and fractionation of solid phases, allochthonous, coming from the coast, as Strakhov (1976₂, p. 201) has it. The main feature of oceanic sedimentation, setting it apart from the continental, is the decisive role of organisms also determining to a considerable extent the course of terrigenous process in the pelagic zone. Combination of bioassimilation, biofiltration, and sorption is different in different climatic zones, thereby determining to a considerable extent the details of processing, transportation, and deposition both of the biogenous material proper and the terrigenous material.

"Hydrodynamic Concept" and the Actual Mechanism of Distribution of Terrigenous Material in the Oceans

We remind that the "hydrodynamic concept" of N. M. Strakhov was worked out also by M. V. Klenova, some 30 years ago, largely on the basis of study of the shallow seas: Barents, White, and others. To quote Klenova (1948, p. 221), "The halistatic zones are reflected in sedimentation maps as ooze and clay-ooze deposits. The dynamic map of currents and map of mechanical composition of sediments are mutually controlling. The bottom composition reflects only the substantial consistent changes in conditions rather than incidental minor fluctuations. The sediment is a projection of hydrodynamic conditions of seawater, but a

projection slowly modified with the prevailing hydrogeological environment. As such, it is a secular mean of all its seasonal, nonperiodical fluctuations. The mechanical composition, accurately determined, may constitute a criterion for judging the dynamic maps."

These lines were written when nothing was known of deep-water circulation systems, the many-level structure of oceanic currents, in the absence of methods and apparatus for the study of suspension and deep currents. The dynamic concept was abandoned following the discovery of new facts. It renders that much more startling Strakhov's revival of these views and his astonishment at "such an interpretation not having been registered in the literature."

M. V. Klenova regarded the hydrodynamics as determining only a single indicator of sedimentary material: its granulometric composition. N. M. Strakhov goes farther and says, "Thus, distribution of absolute volumes of all the components — both mineral and biogenous — in oceanic sediments is directly controlled by the hydrodynamics of the surface layers of oceanic waters" (Strakhov, 1976, p. 12).

My earlier article (Lisitsin, 1977) states that distribution of absolute volumes of CaCO_3 , SiO_2 -amorph, Corg, and other biogenous components in sediments of the World Ocean is not hydrodynamically controlled, and that these components are not concentrated in an active "circumcontinental zone," as believed by Strakhov; instead, they are controlled by the climatic zonation. Just as different from this concept is distribution of absolute volumes of terrigenous material and its several components: clastic and clay minerals, hydrolyzing elements, and others. Their distribution pattern — both percentage-wide and by absolute volumes — is much more complicated, not associated with circulation of surface waters. It is this complexity that induced Strakhov to write, "Relationship with concrete hydrodynamics of the surface layer completely disappears in distribution of terrigenous material, with the same minerals deposited in dynamically active and the passive zones and halistatic regions" (Strakhov, 1976, p. 8).

Only direct investigations of suspension in oceanic waters and the air above them provide means of tracing the sedimentary material over the entire path of its transportation from the place of its entry from land to deposition at the bottom. It is readily seen that water movement gradually shifts the very fine material from the shelf to pelagic zones of the ocean, to depths of 200–500 m, forming long trains or tongues and "clouds" in the upper part of the continental slope (Lisitsin, 1961, 1974). Thus, the bulk of terrigenous material sinks below the surface circulation system as early as along the oceanic periphery, short of the pelagic zone. Farther out in the pelagic zone, it sinks even deeper, into the intermediate, deep, and bottom waters, so that the main transfer of sedimentary material takes place beneath the surface circulation system (Fig. 1).

According to present hydrogeological data, surface circulation, consisting of cyclonic and anticyclonic systems, is replaced at a depth of 50–200 m by a system of intermediate waters, followed by that of deep waters and then by bottom water circulation. Circulation of these water masses varies from place to place. Currents counter to the surface ones are particularly well developed at the intermediate depths, e.g., the Cromwell, Lomonosov, and Tareev countercurrents of the equatorial zone. A. S. Monin et al. (1974) stated that circulation of deep and bottom waters largely is counter to that in surface waters, both in direction and velocity. The velocity rises slightly at the approach to the bottom, and the flow lines tend to follow the bottom relief isobaths. The change from surface circulation to that at depths occurs at 1–2 km below the surface (Monin et al., 1974). Thus, circulation within most of the water mass (3–5 km) differs from the surface circulation and may even proceed in a different direction.

The existence of synoptic eddies, originating in the ocean and corresponding to atmospheric cyclones and anticyclones has now been established along with a small- and medium-scale variability of the ocean: seasonal, annual, and others (Monin et al., 1974).

The inconsistency of Strakhov's dynamic concept is exposed not only by oceanological data but also in the attempts to apply it to any well-known basin within one and the same climatic zone.

The Black Sea would appear to be an ideal site for determining the role of surface currents in distribution of sedimentary material. To quote Strakhov, "Here, water movements at the boundary of the oxygen and hydrogen sulfide zone (15–200 m deep) are too weak to affect appreciably dispersion and distribution of sedimentary material over the bottom. Such an

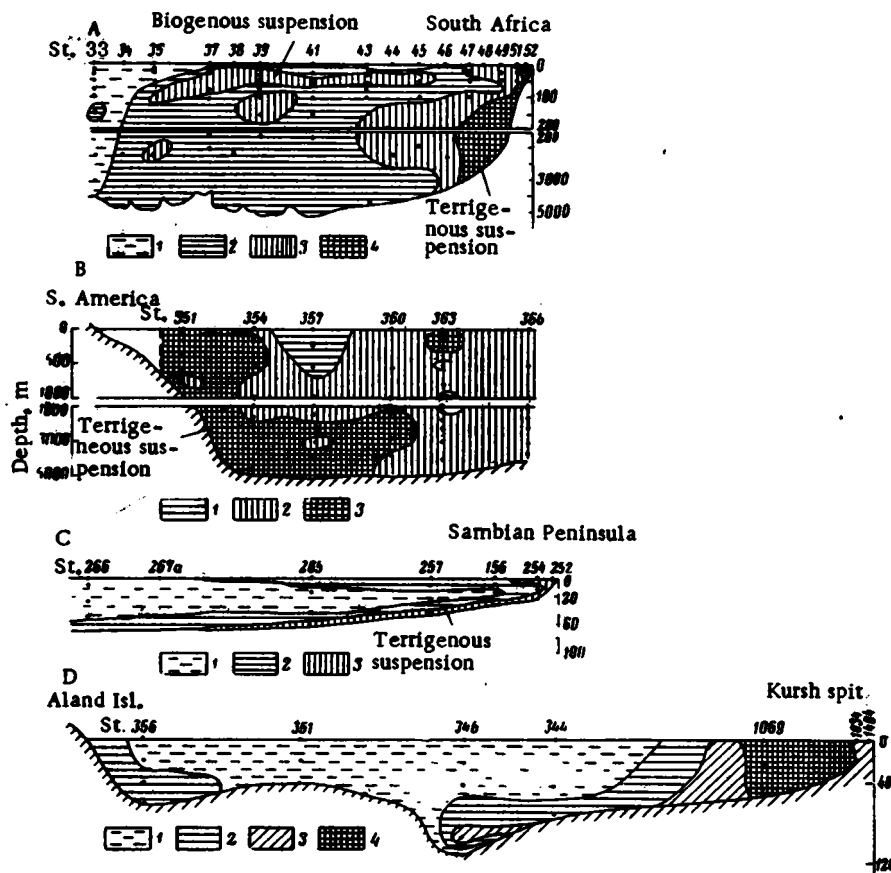


Fig. 1. Quantitative distribution of sedimentary material in marine and oceanic suspension (mg/liter). A) Southeastern Atlantic; section west of Africa, roughly 5° S. lat. Content: 1) <0.5; 2) 0.5-1.0; 3) 1-2; 4) >2; dots) sampling points. B) Western Atlantic; section east of South America. Content: 1) <1; 2) 1-2; 3) >2. C) Baltic Sea, section west of Klaipeda. Content: 1) <1; 2) 1-2; 3) 2-3. D) Changes in content of terrigenous particles in Baltic Sea suspension, section west of the Kursh spit to Aland Island (data of O. G. Pustel'nikov, cited from Lisitsin et al., 1975). Content of terrigenous material (% of suspension): 1) <20; 2) 20-50; 3) 50-80; 4) >80. Dots) Sample points.

effect is produced in the Black Sea only by water movement in the upper dynamically active zone, 50-70 m thick" (Strakhov, 1961, p. 634).

The most convenient indicators of sedimentary material migration are the most mobile clay and clastic minerals and also the geochemical indicators (hydrolyzer elements). Correlation of the system of Black Sea surface currents (Dobrovol'skiy and Zalogin, 1965) with distribution of sedimentation rates (and absolute volumes) for clay and clastic materials and hydrolyzer elements (Fig. 2) leads to the conclusion that the course of the natural process does not support Strakhov's view of a special role for surface water circulation. In these maps, the isolines and boundaries usually intersect the direction of the currents rather than conform to it. This may be due to some special conditions prevailing in the Black Sea and absence elsewhere.

Another illustrative region is Bay of Bengal, Indian Ocean, which receives 1451 million tons of terrigenous material annually, brought in by the Ganges and the Brahmaputra rivers. There are adequate hydrogeological observations and data bearing on distribution of suspension and sediments, including such indicators of terrigenous material distribution as clay and clastic minerals, hydrolyzer elements, and others (Fig. 3).

The main direction of movement for minerals in suspension and in bottom sediments is from north to south, from the Ganges mouth, i.e., across the surface circulation system.

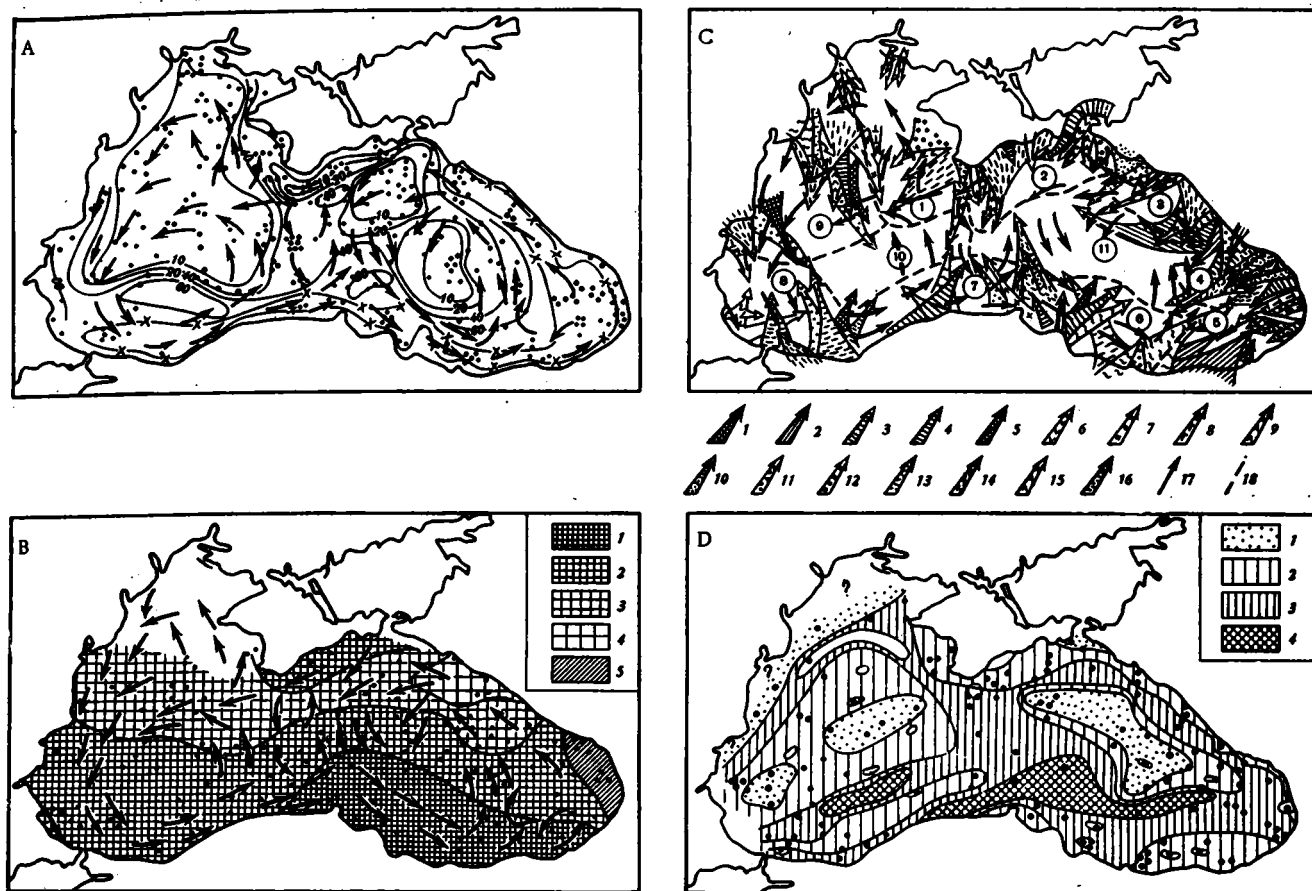


Fig. 2. Sedimentation rates in the Black Sea; distribution of clay and clastic minerals and titanium, correlated with surface waters circulation. A) Sedimentation rates for surface layer of sediments (cm/1000 years). Arrows fly with surface currents (Shimkus et al., 1975). B) Distribution of montmorillonite in fraction <0.001 mm, %: 1) 50-70; 2) 30-50; 3) 20-30; 4) <20 ; 5) zone of diversified contents (Butuzova et al., 1975). C) Regions and paths of migration for clastic minerals (Trimonis, 1975): 1) monoclinic pyroxenes; 2) rhombic pyroxenes; 3) amphiboles; 4) common hornblendes; 5) epidote; 6) garnet; 7) zircon; 8) tourmaline; 9) rutile, sphene; 10) magnetite; 11) ilmenite; 12) limonite-hematite; 13) biotite; 14) quartz; 15) feldspars; 16) muscovite; 17) surface currents; 18) regional boundaries. Terrigenous-mineralogical regions (encircled numerals): 1) West Crimean; 2) Crimean-Kerch; 3) North Caucasian; 4) South Caucasian; 5) Caucasian-Anatolian; 6) East Anatolian; 7) West Anatolian; 8) Bosphor; 9) Danubian; 10) western open sea reaches; 11) eastern open sea reaches. D) TiO_2 distribution in Black Sea sediments, as converted to carbonate-free substance, %: 1) <0.7 ; 2) $0.7-0.8$; 3) $0.8-0.19$; 4) >0.9 (Strakhov, 1976). In all the maps, surface currents' representation after Dobrovolskiy and Zalogin (1965).

Cross sections of suspension distribution, drawn every 4 years, and representing a sort of snapshot of transportation process for sedimentary material in deep waters, show that the bulk of terrigenous material is shifted outside the surface circulation layer, in deep and bottom waters, as corroborated by mineralogical study of clastic and clay minerals and hydrolyzer elements.

Quite obviously, surface circulations in the Black Sea and Bay of Bengal are not responsible for the pattern of terrigenous material distribution. Many other examples can be cited, but their evidence is essentially the same: distribution of terrigenous material over the oceans is not controlled solely by surface water circulation; and the concrete pattern of distribution for suspension and the terrigenous fraction of bottom sediments is much more complicated.

Particularly fruitful in this connection is the study of suspension in oceanic deep reaches, initiated by the Oceanology Institute some 25 years ago, and now consisting of an in-

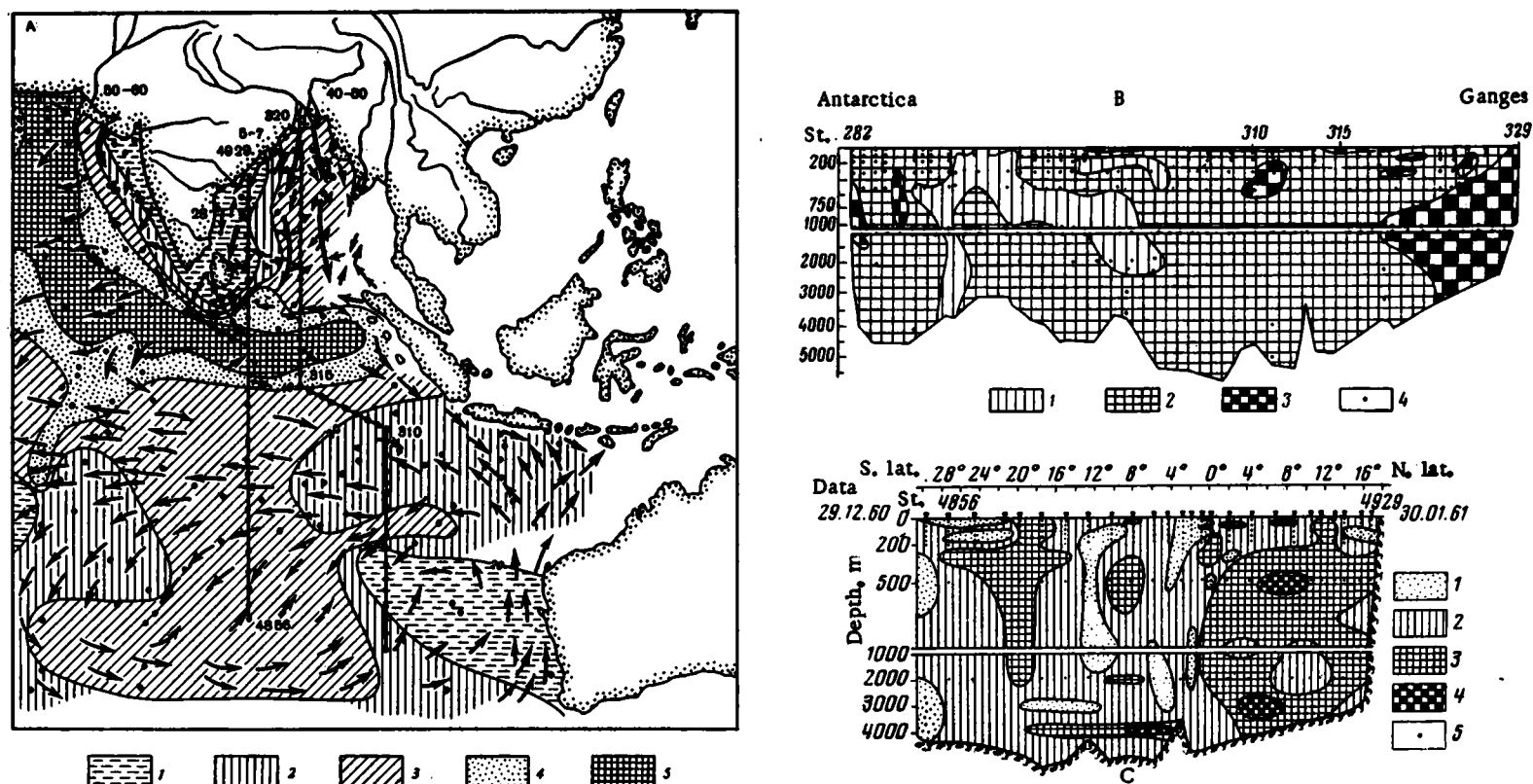


Fig. 3. Distribution of clay minerals in bottom sediments and of suspension material at depths. Also surface currents in the northern part of the Indian Ocean and Bay of Bengal. A) Distribution of illite, less-than-2- μ fraction (Goldberg and Griffin, 1970). Content, %: 1) 1-20; 2) 20-30; 3) 30-40; 4) 40-50; 5) >50. Dots mark stations. Figures near river mouths — illite content in river suspension, %. Arrows fly with surface currents. Lines mark cross sections of suspension distribution. B) Distribution of sedimentary material in suspension along cross section from the Ganges to Antarctica, as indicated in A; in mg/liter (Lisitsin, 1974); 1) <1.0; 2) 1.0-2.0; 3) >2.0; 4) sampling points. C) Same along meridional section from India to 30° S. lat., in mg/liter: 1) <0.5; 2) 0.5-1.0; 3) 1.0-2.5; 4) >2.5; 5) sampling points (Lisitsin, 1974).

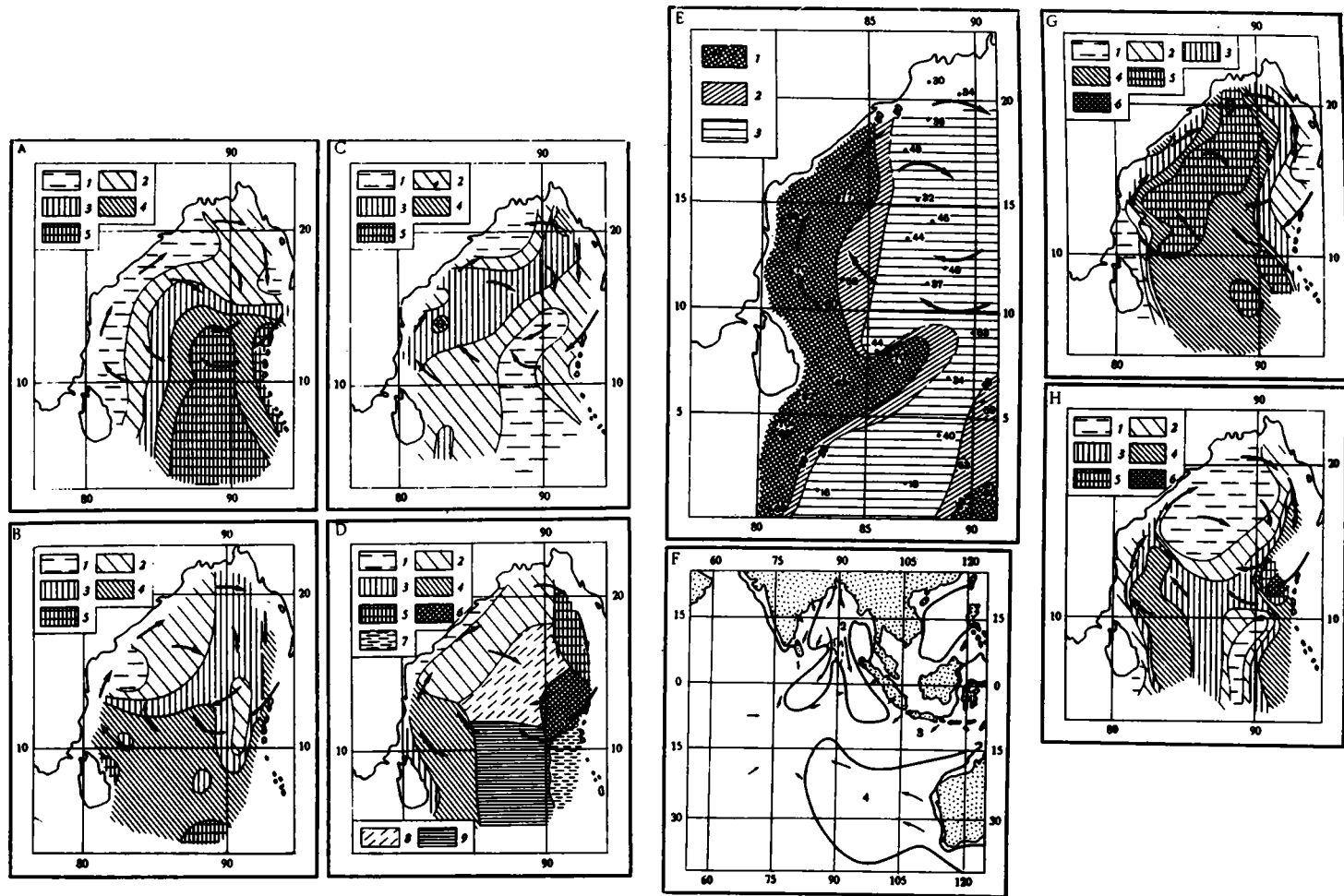


Fig. 4. Distribution of clay and clastic minerals in bottom sediments of the northern part of the Indian Ocean and Bay of Bengal, as compared with surface currents. A) Calcium carbonate in sediments of Bay of Bengal, % by weight: 1) <1.0; 2) 5-10; 3) 10-25; 4) 25-50; 5) >50. B) Hornblende, % heavy subfraction, coarse silt fraction: 1) <5; 2) 8-10; 3) 10-20; 4) 20-40; 5) >40. C) Epidote, % of heavy subfraction: 1) <1.0; 2) 1.0-2.5; 3) 2.5-5.0; 4) 5-10; 5) >10. D) Regions of clastic minerals: 1) coastal Eastern Ghats; 2) deep-water, Eastern Ghats-Ganges delta; 3) coastal Karmandel-Ceylon; 4) deep-water Karmandel-Ceylon; 5) Aracan; 6) North Andaman-Nicobar; 7) South Andaman-Nicobar; 8) North-Central Bay of Bengal; 9) South-Central Bay of Bengal. E) Distribution of smectite in sediments of western Bay of Bengal, % of dry residue: 1) <50; 2) 50-60; 3) >60 (Venkatarathnam et al., 1976). F) Regions of finely dispersed minerals, and migration routes to sediment of the Northwestern Indian Ocean: 1) Dekkan; 2) Ganges River; 3) Indonesian; 4) Australian aeolian (Venkatarathnam and Biscaye, 1973). G) Feldspar in Bengal Bay sediments, % of heavy subfraction, coarse silt fraction: 1) <5; 2) 5-10; 3) 10-25; 4) 25-50; 5) 50-70; 6) >70. H) Clinopyroxenes, % of heavy subfraction, coarse silt fraction: 1) <1.0; 2) 1.0-2.5; 3) 2.5-5.0; 4) 5-10; 5) 10-20; 6) >20. Note: Winter currents, northern hemisphere, FGAM, Map. 50. A-C, G, and H, after H. N. Siddique, 1966.

dispensable part of analysis of the sedimentation process. Studies in this field have yielded interesting results surprising to the lithologists. It turns out that the actual directions of shifting for sedimentary material, as determined from suspension, differ as a rule from the surface currents, often being counter to them.

I refer here to a recent study of the outer Antilles Ridge, a giant sedimentary body at the Atlantic floor, extending for 1200 km northwest from the Puerto Rican deep-water trench as far as the Great Bahama Shoal (Tucholke and Ewing, 1974). As it turns out, sedimentary material coming from the North American continent, from Canada to the Bahama Shoal, is not carried northeastward by the Northern Tradewind Current and Gulfstream, as it should be expected in the event of surface circulation. It proceeds instead in the opposite direction, i.e., southward. This current is marked mineralogically by the presence of chlorite and micas. As indicated by seismic profiling, it has existed for a long time, at least since the Eocene. As a consequence, a body of sediments, over 1 km thick, with a volume of some 60,000 km³, has been accumulated out in the open ocean, in an area separated from the effect of the continent by the Puerto Rican deep-water trench. This deep-water countercurrent, carrying the bulk of "marked" sedimentary material from North America, is opposed in bottom layers along eastern shores of South America by a flow of sedimentary material with a quite different composition (from Antarctica). Here, the bulk of sedimentary material is displaced counter to the Brazilian surface current; having covered an immense distance, it reaches the area of the Puerto Rican trench.

The deep currents keep to certain depths. They duplicate all the isobaths' configuration and are known in marine geology as the contour currents. Their velocity in this region is 2-22 cm/sec. Each year brings new data bearing on the very great role, locally definitive, of precisely these, rather than surface currents in pelagic sedimentation.

The current concept of relationship between oceanic sedimentation and the currents — a concept based on direct study of suspension distribution in waters, and direct observations of deep currents (at buoy stations, neutral flotation buoys, and other means) — is substantially different from Strakhov's concept. Displacement of sedimentary material is determined not only by surface currents but by the entire complex multilevel system of currents, with transportation by deep contour and bottom currents becoming more and more important. The role of currents at any given level changes from one part of the ocean to another, making a prediction of total displacement for an individual particle of sedimentary material very difficult, in most instances. For this reason, determination of secular vectors of sedimentary material migration is achieved, as before, by identification of the areas of dispersion for index minerals and also the typical elements and other concrete indicators of sedimentary material — an operation complemented by a study of submarine photographs, observations of currents and other procedures. The picture of sedimentary material displacement solely by surface currents is not realized practically anywhere in the ocean. The actual displacement is much more complicated, spatially inconsistent. Therefore, we take issue with Strakhov's statement that "With reference to the mechanism of sedimentary process, the ocean is a discrete single under all latitudes. It is not affected by humidity characteristics of different climates (which goes without saying). Only the temperature changes, from the high to low latitudes, modify slightly some features of the sedimentary process" (Strakhov, 1976, p. 13). Moisture changes strongly affect salinity of the ocean — a fact well known in oceanology and geography and just as important in zonation of the oceans as evaporation is in zonation of the continents. A combination of salinity and temperature determines the principal properties both of surface and deep waters; their dynamics related to equalization of density of water; stratification, differentiation into water masses and structures, and zonation. The complexity of the actual oceanic picture is related to latitudinal and vertical changes. In other words, it is multilevel, also variable in time. In Strakhov's view, no consideration is given to the known and undisputable changes in the mechanism of processing, transportation, and deposition of sedimentary material related to the latitude.

The low temperatures of Polar regions are responsible for formation of land and oceanic ice. As another result, the role of water decreases to a minimum in processing and transportation of sedimentary material. It is taken over by water in solid state, i.e., ice. In this region of the earth, ice is the principal agent of sedimentation, both on land and in the ocean. The corresponding principal agent in arid regions is wind — not ground winds but the tropo- and stratospheric, with low velocities. The high strength and recurrence of winds over desert sources of sediments, coupled with a high aridity of air,

create a mechanism of long-distance transportation, absent in other zones of the ocean (troposphere and stratosphere transfer). Thus, there is a clean-cut zonation in distribution of the principal mechanisms of processing and transportation of sedimentary material, both over the ocean and on land. The actual diversity of conditions has nothing in common with their alleged uniformity characteristic of the oceans.

The data cited in the present article show that oceanic sedimentation is by no means a simple dispersion of material brought in by the rivers. One cannot subscribe to the simplistic, and contradicted by facts, "hydrodynamic concept" based on a special role of surface currents. Factors controlling the glacial and arid sedimentation in the oceans will be discussed in the forthcoming article.

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DISTRIBUTION OF LEAD IN BOTTOM SEDIMENTS OF THE BLACK SEA

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UDC 551.35:546.81(262.5)

From a study of the distribution of lead in Holocene, Old Black Sea, and New Euxine deposits, similar vertical distributions of this element have been noted in the oxygen and hydrogen sulfide zones of the sea; i.e., it has been found that hydrogen sulfide contamination has no effect on the quantitative relations of lead in sediments of the basin. Distribution of the element in the Black Sea layers reflects a connection between accumulation of the element and the hydrodynamic regime of the basin and also the forms in which it migrates. It has been noted that the absence of lead accumulation in Black Sea concretions is the result both of the specific conditions under which the concretions themselves formed and of the geochemical activity of the element. An important role of diagenetic sulfide formation has been discovered for the geochemistry of lead: the degree of accumulation of the element in iron sulfides depends on the conditions of sedimentation, on the physicochemical environment of the basin.

The purpose of the present work has been to study the distribution of lead in Holocene, Old Black Sea, and New Euxine deposits of oxygen and hydrogen sulfide zones of the sea and also to investigate the participation of lead in the diagenetic processes leading to the formation of iron-manganese concretions and authigenic sulfides.

Data for this investigation have come from samples collected in 1956-1970 from expeditionary ships of the Institute of Oceanology, Academy of Sciences of the USSR. The distribution of lead in the layer of sediments in the Black Sea (Figs. 1 and 2) was studied in 14 cores (132 samples), two of which were from the shallow-water (114 and 126 m) oxygen zone of the sea, the remainder from the hydrogen sulfide zone (from 440 to 2222 m). Iron-manganese concretions and enclosing muds have been studied from six stations (14 samples) in the oxygen zone of the sea along the Crimean coast. For study of the lead distribution in diagenetic iron sulfides, samples of pyrite, magnetic sulfides, and the muds enclosing them (22 samples), kindly supplied to us by G. Yu. Butuzov and I. I. Volkov, were investigated. The lead content was determined by the author by quantitative spectral analysis in the spectral laboratory of the Institute of Geology of the Academy of Sciences of the USSR.

The lithology of the Black Sea sediments, the patterns of their accumulation, and the history of development of the basin during Quarternary time have been studied in detail in the works of N. M. Strakhov, who has shown that Black Sea sediments of different stratigraphi

Institute of Geology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 23-31, November-December, 1977. Original article submitted January 18, 1977.

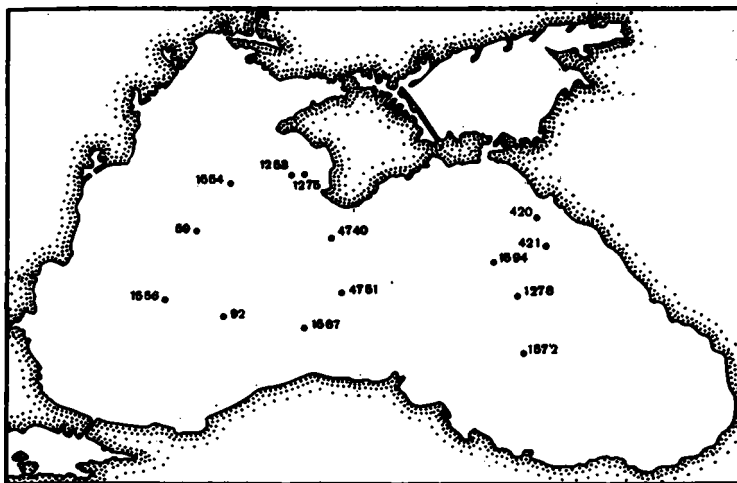


Fig. 1. Scheme of station location.

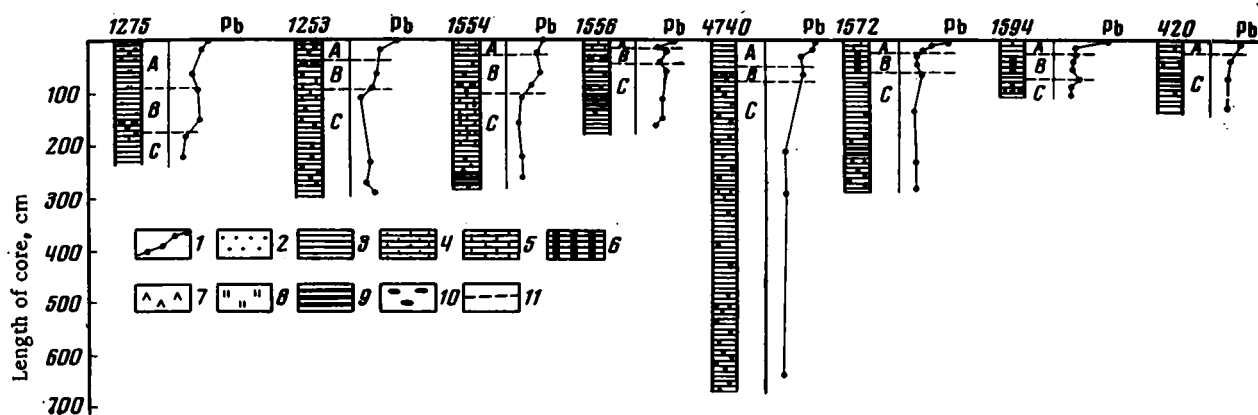


Fig. 2. Vertical distribution of lead in sediments of the Black Sea. 1) Lead content in sediments; 2) silts; 3) clay muds; 4) argillaceous-calcareous muds; 5) calcareous-argillaceous muds; 6) sapropelic muds; 7) patches of pyrite; 8) patches of hydrotroilite; 9) black muds rich in hydrotroilite; 10) Fe-Mn concretions; 11) boundaries of coeval sediments. A) Holocene deposits; B) Old Black Sea deposits; C) New Euxine deposits. Locations of the stations are shown in Fig. 1.

horizons were formed in basins having different hydrodynamic, salt, and gas regimes and differing sharply in petrographic aspect and content of organic material and CaCO_3 (Strakhov, 1963, 1971).

A characteristic feature of the Black Sea deposits is a considerable development of diagenetic iron sulfides in all three stratigraphic horizons. Since hydrogen sulfide contamination may be reflected in the behavior of such a typically chalcophile element as lead, study of its distribution in Black Sea sediments is of great interest for the geochemistry of the element in the sedimentary process.

Cores 108-970 cm in length contain Holocene, Old Black Sea, and, in part, New Euxine deposits. The lead content in the sequence of layers ranges from $3 \cdot 10^{-4}$ to $34 \cdot 10^{-4}\%$ in natural sediment and from $8 \cdot 10^{-4}$ to $41 \cdot 10^{-4}\%$ when recalculated to carbonate-free material (Table 1, see Fig. 2); i.e., the limits of variation are much narrower than in the surface layer of sediments in the Black Sea [from $1 \cdot 10^{-4}$ to $103 \cdot 10^{-4}\%$ (Lubchenko, 1970)].

In examining the vertical distribution of lead in separate cores, a reduction in concentration has been noted in all layers in argillaceous-calcareous and calcareous-argillaceous muds, especially notable in natural sediment [up to $(3-5) \cdot 10^{-4}\%$]. In recalculation of carbonate-free substance the contents level off somewhat, but still high-carbonate muds are generally characterized by reduced concentrations of lead. Only in the surface layer of recent sediments do almost all cores exhibit an increase in lead content regardless of car-

TABLE 1. Lead Content in a Section of Holocene Sediments of the Black Sea, $10^{-4}\%$

Horizon	Zone and station No.							
	oxygen			hydrogen sulfide				
	1253	1275	1554	1556	4740	1572	1594	420
Holocene	$\frac{23-36^*}{29}$	$\frac{21-39}{30}$	$\frac{24-28}{26}$	$\frac{28}{28}$	$\frac{26-37}{33}$	$\frac{18-38}{27}$	$\frac{14-41}{24}$	$\frac{23}{23}$
Old Black Sea	$\frac{19-22}{21}$	$\frac{24-28}{25}$	$\frac{20-26}{23}$	$\frac{15-23}{29}$	$\frac{27}{27}$	$\frac{14-15}{15}$	$\frac{16-21}{18}$	Not de- posited
New Euxine	$\frac{14-19}{14}$	$\frac{13-15}{14}$	$\frac{10-13}{11}$	$\frac{17-19}{18}$	$\frac{14-17}{15}$	$\frac{12-16}{14}$	$\frac{16-16}{16}$	$\frac{14-15}{15}$

*The numerator shows the minimum and maximum lead content, the denominator the average.

TABLE 2. Average Lead Content in Different Stratigraphic Horizons of the Black Sea, $10^{-4}\%$

Type of deposit	Oxygen zone	Hydrogen sulfide zone
Holocene	30 (36)*	24 (27)
Old Black Sea	23	20
New Euxine	14	15

*The lead content in the surface layer with consideration of grab samples is shown in parentheses.

TABLE 3. Lead Content in Size Fractions of Black Sea Sediments, $10^{-4}\%$

Station No.	Horizon, cm	Fraction, mm		
		<0,001	0,01-0,001	0,1-0,01
8	0-3	55	29	3
11	0-5	27	33	—*
13	0-3	58	31	5
14	0-3	80	34	—
16	0-5	65	26	—
18	0-5	40	18	—
24	0-3	27	18	—
33	0-5	40	17	4
4752	464-470	28	10	—

*No fraction.

bonate content. Since calcium carbonate in the sediments is only a diluent, we have recalculated all results of analyses to carbonate-free substance.

In the shelf oxygen zone of the sea, aspects of the lead distribution in the sediments were studied at stations 1253 and 1275 (see Table 1 and Fig. 2). In Holocene deposits, represented by clay muds with small admixtures of silt and shell fragments, with iron-manganese concretions in the upper oxidized zone and disseminations of hydrotroilite in the reduced sediments, the lead content ranges from $21 \cdot 10^{-4}$ to $39 \cdot 10^{-4}\%$, averaging $30 \cdot 10^{-4}\%$. The maximum concentrations of the element are found in the upper oxidized film enclosing the concretions.

In Old Black Sea clay muds having a small number of sapropel layers and thin films of hydrotroilite, the lead content ranges from $19 \cdot 10^{-4}$ to $26 \cdot 10^{-4}\%$, averaging $23 \cdot 10^{-4}\%$. In New Euxine sediments the lead content declines sharply, ranging from $14 \cdot 10^{-4}$ to $19 \cdot 10^{-4}\%$ in clay muds and from $9 \cdot 10^{-4}$ to $10 \cdot 10^{-4}\%$ in argillaceous-calcareous muds. The average lead content for the New Euxine sequence is $14 \cdot 10^{-4}\%$.

TABLE 4. Lead Content in Concretions and Enclosing Muds of the Black Sea

Station No.	Horizon, cm	Characteristics of sample	In carbonate-free substance, 10 ⁻⁴ %	MnO	Fe ₂ O ₃ wt. %	CaCO ₃
4	—	Concretion	19	9.5	32.90	19.87
	—	Concretion	17	7.45	37.15	11.10
6	2-4	Gray clay mud	28	N.d.	N.d.	23.86
	15-20	Gray clay mud with black inclusions	27	0.03	5.38	19.50
	—	Concretion	18	2.95	47.10	9.30
7	2-5	Yellow-brown clay mud	29	N.d.	N.d.	21.37
	18-22	Gray clay mud	26	N.d.	N.d.	22.27
	—	Concretion	17	12.66	31.44	12.50
11	3-5	Gray clay mud with cream-colored tone	33	0.04	4.98	25.28
	18-22	Gray mud with light blue tone; contains black layers	27	0.05	6.13	24.87
	—	Concretion	14	13.13	29.80	13.90
12	2-4	Gray clay mud	26	N.d.	N.d.	24.20
18	18-20	Gray mud; contains black layers	24	0.05	6.26	23.82
23	—	Concretion	11	6.93	41.94	9.05

Note: N.d.) Not determined.

Thus, a reduction in lead content from recent sediments to New Euxine sediments is noted in the investigated cores of the oxygen zone. The highest values of lead content are found in the upper oxidized layer of Holocene sediments.

In deep-water sediments of the hydrogen sulfide zone, the behavior of lead in vertical distribution has been studied in 12 cores. We have examined the distribution of the element in the six most typical sections, where stratification is reliably observed and the samples are from coeval intervals.

The lead content in argillaceous, argillaceous—calcareous, and calcareous—argillaceous muds of the Holocene deposits ranges from $14 \cdot 10^{-4}$ to $41 \cdot 10^{-4}\%$. In Old Black Sea sediments the range narrows to $14 \cdot 10^{-4}$ to $27 \cdot 10^{-4}\%$. In sapropelic muds of the Old Black Sea sediments no notable increase in lead concentration has been observed: as compared with argillaceous muds, the concentration is lower (core 1554), but as compared with argillaceous—calcareous muds it is higher (core 1556). Although there is no direct connection between the amount of organic material and the lead content in the sediments, we cannot completely eliminate the possibility that lead has been sorbed by organic material. Since the content of organic material controls the sulfide-forming process (Strakhov, 1963, 1971) and sapropelic layers are always rich in pyrite, it is extremely difficult to mark the limits of the effect of C_{org} and iron sulfides on the concentration of lead in the sediments as well as on the concentrations of other trace elements (Volkov and Fomina, 1971).

The lead content in clay deposits of the New Euxine horizon ranges from $10 \cdot 10^{-4}$ to $19 \cdot 10^{-4}\%$. In layers of black mud from New Euxine sediments having a large number of nodules and concretions of iron sulfides, the concentrations of lead remain at a level normal for this horizon.

Thus, in the investigated cores from the hydrogen sulfide zone, the average lead content for the stratigraphic horizons exhibits an identical character in the distribution of the element. Also, as in cores of the oxygen zone, the average lead content increases from New Euxine sediments to recent sediments, reaching a maximum in the sediment surface layer.

Aspects of lead accumulation in different layers of Black Sea sediments becomes still clearer when we calculate average concentrations of the element in Holocene, Old Black Sea, and New Euxine sediments for the oxygen and hydrogen sulfide zones as a whole (Table 2). The data in Table 2 show that the distribution of lead in the sequence of sediments of the oxygen and hydrogen sulfide zones is the same in each: a continuous increase in content of the element is observed from New Euxine sediments to Holocene sediments, and the average concentration remains essentially unchanged.

TABLE 5. Vertical Distribution of Lead Contents in Sediments of the Oxygen Zone of the Black Sea, $10^{-4}\%$

Station No.	Horizon, cm	Characteristics of sample	In carbonate-free substance, $10^{-4}\%$	CaCO ₃	C _{org} wt. %
1275	0-1 _A	Clay mud, semiliquid, yellowish brown; contains concretions	38	25.8	1.49
	2-5 _A	Gray clay mud; has fine individual inclusions of hydrotroilite	31	23.0	1.73
	18-22 _A	Gray clay mud; contains numerous fine hydrotroilite inclusions	26	18.9	1.37
	60-68 _A	The same	20	20.9	1.30
	107-117 _B	Dense clay mud, gray; contains rare and fine admixtures of hydrotroilite	23	8.2	1.77
	150-158 _B	Sapropelic mud with clay admixture	24	12.2	3.66
	179-184 _C	Light gray calcareous-argillaceous mud	11	49.0	0.54
	223-230 _C	Light gray clay mud	12	21.4	0.30
	0-0.5 _A	Clay mud, yellowish brown, semiliquid; contains concretions	32	23.6	1.91
	1-3 _A	Gray clay mud with greenish tone, grumous structure	29	23.4	1.77
1253	18-20 _A	Gray clay mud; contains a large quantity of hydrotroilite admixture	22	24.2	1.81
	20-30 _A	The same	24	26.0	1.30
	64-68 _B	Gray clay mud with greenish tone	21	9.9	2.01
	86-91 _B	The same	18	29.8	1.59
	107-110 _C	Light gray calcareous-argillaceous mud	9	53.7	0.53
	230-235 _C	Gray clay mud; contains numerous layers of hydrotroilite	17	9.6	0.34
	273-277 _C	Very dense, black clay mud	14	8.6	0.33
	290-298 _C	The sequence of mud is found to contain semisolid nodules and small concretions of iron sulfides. Gray clay mud, viscous; has individual films of hydrotroilite	20	11.5	0.42

Note. A) Holocene deposits; B) Old Black Sea; C) New Euxine.

This means that hydrogen sulfide contamination, changing the forms in which the elements occur and the mechanism of their introduction into the bottom water (Strakhov, 1971), does not affect the quantitative content of lead in the sediments, an element with clearly expressed chalcophile properties. There is obviously a single cause: an extremely low concentration of lead in the water of the Black Sea. We do not have actual determinations of lead in this water at our disposal, but the average concentration of the element in seawater is known to be $1 \cdot 10^{-8}$ g/liter (Vinogradov, 1967). The content of dissolved lead in stream waters of the Black Sea basin ranges from $9 \cdot 10^{-8}$ to $160 \cdot 10^{-8}$ g/liter, averaging $58 \cdot 10^{-8}$ g/liter (Lubchenko and Belova, 1973). In modeling the natural process of sulfide accumulation (Rozhkova et al., 1970), lead sulfides, even in colloidal form, do not precipitate at concentrations below $5 \cdot 10^{-4}$ g/liter. In addition, the solubility of heavy-metal sulfides in the presence of hydrogen sulfide and at a pH of 7.4-8.0 increases appreciably because of the formation of various ionized soluble complexes (Rafal'skii, 1966).

The distribution of lead in Black Sea sediments reveals a connection between the element and changes in the hydrodynamic regime of the basin and also forms in which it migrates. In the Black Sea a decline in sedimentation rate, a weakening of the hydrodynamic regime of the basin (Arkhangel'skii and Strakhov, 1938), took place in late New Euxine time, and the content of lead in the sediments increased at the same time. This pattern follows logically from the restriction of lead to the finest fraction of stream suspension for rivers of the Black Sea basin (Lubchenko and Belova, 1973), and it is confirmed by fraction analysis for

TABLE 6. Lead Content in Sulfides and Enclosing Muds of the Black Sea

Type of sediment	Station No.	Horizon, cm	Characteristics of sample	Pb $10^{-4}\%$	Concn. coeff.
Holocene deep-water	711	0-15	Pyrite	45	3.0
Old Black Sea deep-water	1572	55-70	Homogeneous gray clay mud	15	5
			Pyrite	93	
New Euxine deep-water	1572	125-128	Gray clay mud with brownish tone	16	5.0
			Magnetic fraction of sulfides	75	
New Euxine deposits of the continental slope	1572	188-190	Gray clay mud	15	6.6
			Magnetic fraction of sulfides	79	
	67	170-270	Gray clay mud	12	5.1
			Pyrite	76	
	4740	220-380	Gray clay mud	15	6.0
			Pyrite	125	
	1635	1-16	Drak gray clay mud	20	0.18
			Pyrite	5	
	1665	2-17	Plastic gray clay	27	0.26
			Pyrite	4	
	1666	2-12	Dense gray clay mud	15	0.46
			Pyrite	7	
	1679	2-15	Dense viscous gray clay mud	15	0.47
			Pyrite	10	
	1679	2-15	Very dense viscous gray clay	21	0.24
			Magnetic fraction of sulfides	5	
			Very dense viscous gray clay	21	

the sequence of Black Sea sediments (Table 3): in all cases, a maximum concentration of lead is observed in the fine pelitic fraction. Therefore, the less active hydrodynamic regime, as compared with the New Euxine, in which the Old Black Sea sediments accumulated, and, especially, in which Holocene sediments accumulate, favored the deposition of coarser particles in the near-shore zones and fine particles in more pelagic zones, leading to enrichment of lead in muds of Holocene and Old Black Sea horizons.

The distribution of lead in Black Sea iron-manganese oxide concretions and the enclosing muds was studied at six stations in the shallow-water oxide zone of the sea along the Crimean coast. In contrast to oceanic sediments, lead has not accumulated in iron-manganese oxide concretions of the Black Sea (Table 4). The lead content in the concretions ranges from $11 \cdot 10^{-4}\%$ to $19 \cdot 10^{-4}\%$ (in carbonate-free substance of the sediment). The concretion coefficient relative to the enclosing sediments is always less than unity.

Unfortunately, in studying the concretions we did not have at our disposal samples of mud from the oxidized layer containing the concretions themselves. Therefore, in order to determine the participation of lead in the redistribution process as a result of redox processes, we have used data from cores of the oxygen zone (Table 5). As the data in Table 5 show, a small increase in lead is observed in the oxidized layer of sediments (up to $(32-38) \cdot 10^{-4}\%$). Lead enriches the oxidized layer to the same extent as other trace elements, the distribution of which, during formation of Black Sea concretions, has been studied by Volkov (Volkov and Sevast'yanov, 1968).

Why then is lead, which takes part in the redistribution processes of elements, not concentrated in concretions of the Black Sea? This is explained by the negligible role of mobile forms of lead in the sediments, which follows from a number of causes. First, the iron-manganese concretions of the Black Sea form in the shallow-water zone, where the amount of the material in reactive form is minimal. Another cause is the chalcophile properties of lead, manifested in the distinctive conditions of the environment of the Black Sea de-

posits. In the reducing layer of sediments immediately beneath oxidized mud, lead, like copper (Volkov and Sevast'yanov, 1968), is bound in a relatively insoluble sulfide [the solubility of PbS is $2.5 \cdot 10^{-27}$, of CuS $6.3 \cdot 10^{-36}$ (Lur'e, 1962)] and does not participate further in redistribution processes. This is confirmed also by the fact that in the uppermost layer of reduced mud the concentration of lead increases somewhat ($(29-31) \cdot 10^{-4}\%$).

And lastly, it is necessary to consider the "time factor" in considering the diagenetic redistribution of elements. The degree of accumulation of elements in concretions may also depend on the rate of the concretion-forming processes (Strakhov, 1963; Strakhov et al., 1967). Oceanic concretions differ from Black Sea forms by a much lower rate of formation; consequently, they may be more enriched in all trace elements, even those of low mobility: Zr and Ti.

Thus, the absence of lead accumulation in Black Sea concretions is the result both of specific conditions of formation of the concretions themselves and of the geochemical mobility of the element.

Since Black Sea deposits of the hydrogen sulfide zone are characterized by a high content of iron sulfides, we examined the behavior of lead in sulfides of deep-water deposits (Holocene, Old Black Sea, and New Euxine) and in sulfides of New Euxine sediments of the continental slope. The accumulation of lead in Black Sea sulfides should be expected, since the element should doubtlessly be found in sulfide form under conditions of hydrogen sulfide contamination.

Butuzova (1969), studying iron sulfides from deep-water Old Black Sea and New Euxine deposits, first established a clear affinity of lead, as also of copper, nickel, arsenic, and cobalt, for pyrite and magnetic sulfide forms. In the opinion of the author, epitactic inclusions — microscopic and submicroscopic intergrowths and overgrowths — represent the most likely form for lead as well as copper to occur in sulfides.

According to our data, the lead content in iron sulfides in the deep-water deposits ranges from $45 \cdot 10^{-4}$ to $125 \cdot 10^{-4}\%$, averaging $80 \cdot 10^{-4}\%$. The lead content in muds enclosing the sulfides ranges from $12 \cdot 10^{-4}$ to $20 \cdot 10^{-4}\%$, averaging $15 \cdot 10^{-4}\%$ (Table 6). As seen from the data of Butuzova (1969) and our information, there is no correlation between concretions of lead in sulfides and in the enclosing sediments. But our results attest to the fact that the accumulation of lead in sulfides of different stratigraphic horizons varies somewhat. The concentration coefficient of lead in sulfides relative to the enclosing muds amounts to 3.0 for Holocene deposits, 5.8 for Old Black Sea deposits, and 5.5 for New Euxine deposits.

Lead has not accumulated at all in iron sulfides from the New Euxine sediments of the continental slope: the coefficient of concentration is invariably less than unity. In these sediments one may observe a similarity between lead and copper during diagenetic processes during authigenic formation of sulfides (Volkov and Fomina, 1972).

The sharp enrichment of lead in some iron sulfide nodules and the absence of the element in others are controlled by the conditions and duration of the sulfide-forming processes. Iron sulfides of deep-water deposits of Holocene and Old Black Sea layers were formed in a reducing environment in both the water layer and the sediments, against a background of high quantities of lead in the enclosing muds. Correlation of lead with iron sulfides, which may have nucleated in part in water above the sediment, reaches a maximum in the muds, since the process of sulfide formation takes place chiefly in the sediments and not in water of the hydrogen sulfide zone. Duration of the sulfide-forming process has been expressed in a somewhat lower concentration of the element in the sulfides of recent sediment.

The New Euxine deposits are characterized by a reduced concentration of lead, reaching a minimum in the near-shore parts of the sea. Iron sulfides of the New Euxine layer did not form in situ during diagenesis of these sediments. Sulfides of deep-water deposits of New Euxine beds were formed through diffusion of hydrogen sulfide, sulfur, and colloidal iron monosulfide from the overlying sediments by means of processes prolonged in time. In the region of steep continental slope, initially oxidized New Euxine sediments are exposed on the surface. Through hydrogen sulfide contamination of the water layer they have been reduced and the formation of sulfides has begun. But, since the concentration of lead in the enclosing muds is low and the formation of iron sulfides takes place quickly, lead does not accumulate in these sulfides.

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Formation of the bulk of residual and many sedimentary rocks and ores and also the origin and development of life on the earth are associated with weathering processes. Percolating hydrolysis is distinguished as the basic process of humid weathering, decomposition of silicates, and the formation of clay, bauxite, and other residual ores. Current diagenesis, similar to percolating diagenesis, culminates on the floor of through-flowing basins with silica-free weakly acidic water. The principal chemical processes in the weathering zone relative to categories of complexity of the compounds that form take place in two opposite directions: on the one hand, rather complex framework silicates are destroyed and generally more simple oxides, soluble salts, and sheet silicates are formed; on the other, from the mobile products of weathering and volcanism, with the participation of carbon, much more complex compounds have appeared since the dawn of earth history — organic material; organic life arose and has continued to develop. The weathering process is considered to be not only destruction but creation through destruction, and, in relation to lithology, creation of the weathering crust and sedimentary material.

Chemical Weathering

M. S. Shvetsov in his textbook "Petrography of Sedimentary Rocks" assigned great significance to processes of chemical weathering. He wrote that, as a result of these processes, "...complex molecules from the weathering of magmatic silicates are gradually restructured and then completely destroyed, and their component parts go into solution, from which they are commonly precipitated immediately, forming new minerals" (1958, p. 19). In this process the mobile components — K, Na, Ca, and Mg — are removed in true solutions far away to the sea, but the much less mobile components — Si, Fe, Al, and Mn — accumulate in place, forming clays and various ores. Shvetsov noted repeatedly that primary silicates are decomposed or disintegrated during weathering.

Among the various processes of chemical weathering we now distinguish oxidation of low oxide forms of iron and manganese, free and sulfide forms of sulfur, coal and organic compounds; decomposition of silicates; solution and removal of soluble components; and the formation and accumulation of minerals and organic matter that are stable in any specific weathering environment.

Many definitions of weathering are to be found in Soviet and foreign literature. Usually weathering is defined as the destruction or change and destruction of minerals and rock under conditions at the earth's surface because of chemico-mechanical action of the atmosphere, groundwater, surface water, and organisms.

From the viewpoint of geology and lithology, it is more nearly correct to consider weathering to be not only destruction but also creation of solutions, minerals, rocks, ores, organic matter, and organic life, a process of creation through destruction. These two represent an indivisible process, as inseparable as the left and right sides of an equation.

The names of the weathering process — destruction or creation — are generally assigned subjectively, depending on the value of the product obtained. If the product is less valuable than the original we then speak of destruction; if it is more valuable we speak of creation.

The problem of destruction of one category of structural complexity and formation of another is also related to various concepts of the weathering process. Relative to this, Logvinenko (1974, p. 16) has written: "In most cases during weathering, changes in more com-

Institute of Geology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 32-43, November-December, 1977. Original article submitted November 12, 1975.

plex compounds have taken place and simpler compounds have formed..." But in nature, along with simpler compounds, many more complex compounds arise, particularly organic matter and living substance. Although these constitute a "minority of cases," they should not be neglected, especially in view of the enormous role they play in weathering and in the life of mankind.

The most complex terrestrial substances — protoalbumin, albumin, and living organisms — formed in ocean from mobile products of weathering and volcanism. This took place 3.5–4 billion years ago, and since that time organic life has existed and developed continuously to the present time. Consequently, organic life against the background of earth geologic history is a distinctive chain reaction or chain process (Bushinskii, 1971).

Plants, feeding on mineral substances, create from them living substance. In turn, living organisms, products of their life activity, and dead organic matter prove to have a great influence on weathering processes. Thus, in pre-Devonian time, when vegetation on land was extremely poor or absent, weathering was accompanied by the accumulation of red ferruginous rocks. Beginning with the Carboniferous, along with the continuing red weathering material, white weathering products appeared in the form of white kaolin.

The concept of the weathering process differs from various writers, and it is not always correctly understood even by prominent geologists. It is especially unfortunate to find errors and inaccuracies in good textbooks. Let us consider some examples.

"Chemical weathering leads to change in minerals of the deep-seated zones of the earth, which have arisen under conditions of high pressure and high temperature, converting them to minerals stable on the earth's surface" (Logvinenko, 1974, p. 16). Actually, as Shvetsov (1958) has written, during chemical weathering it is not an alteration of minerals that occurs, but a destruction, not their transformation to new minerals but the formation of new minerals from solutions. This is clearly seen from the following. The earth's crust consists chiefly of framework aluminosilicates and iron silicates. These are destroyed during chemical weathering. Layered aluminosilicates and iron silicates and various oxides are formed from relatively immobile products of decomposition and water, but mobile products are carried away by streams and, together with volcanic products, form the salt mass of the ocean. The essence of chemical weathering consists in this.

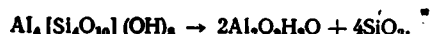
The idea of destruction of framework silicates and the formation from them of clay minerals through a stage of solution was proposed long ago (Bushinskii, 1946; Shvetsov, 1958). This was demonstrated by the fact that clay particles, even those formed from a single crystal, have various optical orientations. The transition of aluminum from tetrahedral coordination in framework silicates to octahedral coordination in layered silicates now attests to this process (Rus'ko, 1972). By means of the electron-microscope method of vacuum ornamentation in combination with microdiffraction, Chekin, Fin'ko, and Samotoin (1974) succeeded in tracing the process of destruction of feldspars and the formation of clay minerals in kaolinitic weathering crusts. In these crusts microcline and muscovite have been replaced by kaolinite, but oligoclase by halloysite. This replacement has taken place without participation of any intermediate minerals; i.e., it has taken place through a solution stage. Small crystals of kaolinite and halloysite have grown epitactically on planes of primary minerals in various but strictly definite forms. The structure of the primary mineral in some cases strongly influenced crystallization of the clay minerals; in others the effect of the weathering environment was dominant. From these data it follows that in the weathering process feldspars are not "transformed," as the authors wrote in the title of their article, but are destroyed. During lateritic weathering, destruction of feldspars also takes place, but with the formation of alumogel, from which crystals of gibbsite grow.

The decomposition reaction of feldspar with participation of CO_2 as cited by A. I. Tugarinov (1973, p. 157) is incorrect:



The components on the left-hand side of the reaction equation here do not move to the right, and the components of the right-hand side do not accumulate and cannot coexist, since they react with each other. But the principal fact is that this reaction does not take place if there is no introduction of large quantities of water and removal of the dissolved products: silicon and potassium compounds.

Even experimental geologists, in explaining the process of laterization, usually ignore the role of water percolation and the removal of dissolved components. Thus, Logvinenko (1974, p. 21) wrote: "In countries with moist tropical and subtropical climate, further decomposition of kaolinite takes place with the formation of free oxides of aluminum, iron, and silicon (lateritization process):



But this reaction does not take place in nature. During weathering kaolinite does not decompose without the participation of water. In the laterization process nowhere has the joint accumulation of silica and alumina been observed. Aluminous laterites are at once distinguished by the negligible silica content. Decomposition of kaolinite in a nearly neutral environment takes place only through percolating hydrolysis: energetic removal of silica from the sphere of reaction (Bushinskii, 1971, 1975). Concerning the formation of free ferric oxides, as Logvinenko has written, the process is impossible, since iron is not contained in kaolinite.

Another error of Logvinenko is his representation of SiO_2 as practically immobile, and Fe, Al, and Ti as weakly mobile (1974, p. 21), a conclusion uncritically cited by other writers. Actually, during humid-climate weathering in an acidic environment it is just the opposite: Fe^{3+} , Al, and Ti are the least mobile, and silica is weakly mobile (Lisitsyna, 1973). This is clearly demonstrated by the chemical composition of ground- and surface waters in which the content of dissolved silica generally ranges from 1 to 40 mg/liter and the total amount of dissolved oxides of Fe^{3+} , Al, and Ti rarely reaches 1 mg/liter. Correspondingly, quartz also is not "very stable," but corrodes during lateritization and is replaced by more stable minerals: gibbsite, kaolinite, goethite, and hematite. Also untrue is the statement of Logvinenko that clay minerals are very stable. In nature, of these only kaolinite or minerals of the kaolinite group are very stable. Stability of the other clay minerals is not high; in the weathering crust they are destroyed, disappearing upward, not even reaching the bauxite zone. These minerals are not associated with sedimentary bauxites except in rare examples. This is explained by the fact that the formation of many sedimentary bauxites is also related to hydrolysis, but in through-flowing water on the floor of an aqueous basin.

Among foreign geologists, one of the most prominent in the field of weathering processes is W. D. Keller (1957, 1959). To this investigator belongs the graphic expression that, relative to feldspars and other rock-forming silicates, water is apparently enemy No. 1. For an understanding of the weathering process, Keller proposed the law of rock and mineral stability. In accord with this law, rocks and minerals are stable only under conditions of their formation, and in the measure that these conditions change the rocks and minerals change to other varieties that are relatively stable under the new conditions. In a somewhat different formulation, we discussed the conditions of stability thus: "Minerals are most stable and are most readily formed from aqueous solutions at pH and oxidation-reduction values that are the same as or very similar to those at which they form during their hydrolytic dissociation" (Bushinskii, 1946, p. 11). Producing some specific reaction with the medium, minerals, as it were, preserve themselves from further decomposition. Changes in this reaction lead either to further decomposition or to transformation of the minerals. Especially intense decomposition of minerals takes place under conditions of percolating hydrolysis.

The weathering reaction of Keller is given in the following form:



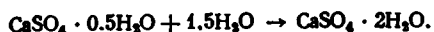
But the components on the right side of the reaction do not accumulate jointly in a lateritic weathering crust. Further, Keller explains that the land is the acidic part of this reaction and the ocean is the alkaline part. In order for the reaction to move toward the right (continuation of weathering), it is necessary that the soluble weathering products be removed from the active system. However, this explanation is not reflected in the reaction described by Keller.

This error in writing the reaction for weathering of silicates is encountered in a number of other foreign and Soviet papers, including my own. It is clearly necessary to have a new fundamental expression for the reaction of silicate weathering, with consideration of percolating hydrolysis.

Percolating Hydrolysis

Hydrolysis is chemical reaction between solid or dissolved substances and water. In addition to water and salts, reactions of hydrolysis may involve acids, alkalies, and organic matter, usually with the assistance of organisms and catalysts. The hydrolysis of salts of strong acids and weak bases is well known. Thus, an acid solution containing ions of Al^{3+} , Cl^- , and H^+ is formed when the salt AlCl_3 is dissolved in water. With dilution of this solution by water, the solution is neutralized; ions of aluminum combine with hydroxyl ions, forming various complex ions and sols, which precipitate in the form of gel. This gel then ages and crystallizes in the form of gibbsite or other minerals. According to this scheme, oxides of iron, titanium, gallium, and other metal-hydrolyzates precipitate from acid solutions.

Examples of hydrolysis of minerals may be seen in the formation of gypsum from mixtures of polyhydrate powder and water and in the conversion of cement mixture to concrete. The first reaction, under normal conditions, takes place in accord with the following scheme:

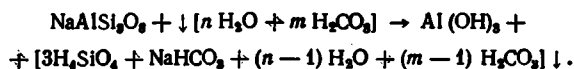


At a temperature of 140°C hydrolysis ceases and dehydration of gypsum occurs: the reaction proceeds in the reverse direction. In the second reaction, tricalcium silicate (a component part of Portland cement) in mixtures with a certain amount of water is hydrolyzed with the formation of a solid dry product. This reaction is also reversible, but its movement in the reverse direction is effected at a higher temperature: about $1450\text{--}1500^\circ\text{C}$. Both of these reactions take place practically to the end without formation of by-products and without introduction of any substance from outside, i.e., in a closed space so to speak.

In nature, however, reactions with silicates in contact with water take place in various systems: closed, open, and intermediate of varying character. Stagnant or slowly percolating groundwater represent a closed or semiclosed system. In such a system, at temperatures up to 100°C , in a near-neutral environment, hydrolysis takes place very weakly, so that silicates remain almost unchanged. This is explained by the fact that minerals, giving up even a negligible part of their components into solution, achieve "equilibrium" with them, so to speak, and are not further decomposed. Thus, for stability of feldspar in the presence of water, it is sufficient if the content of silica in the water is $10\text{--}40$ mg/liter. This concentration exists almost everywhere in groundwater, streams, and seawater; therefore, silicates do not decompose in them or only in very limited amounts. The stability of silicates in contact with water is fostered by the presence also in the water of other dissolved components constituting silicates.

During weathering under humid conditions, the hydrolysis of minerals differs fundamentally from the indicated reactions by the introduction of huge masses of weakly mineralized silica-free rain water and the removal of dissolved products of the reaction with water; i.e., it takes place in an open system. In this system the percolating waters are aggressive because of the absence or negligible amount of silica and other dissolved mineral substances in them. The processes of hydrolysis in such a system are widespread in nature and rather specific. It is therefore appropriate to assign a new name: percolating hydrolysis (Bushinskii, 1971, 1975). Because of percolating hydrolysis of silicates in hot moist climates, argillaceous and other rocks of thick weathering crusts, lateritic or residual iron, manganese, and nickel ores, bauxite and kaolin are formed (Bushinskii, 1975, 1976).

The chemical reactions of silicate hydrolysis during weathering as represented by various writers, as was pointed out above, do not take place and cannot take place. Some writers explain their representations of the reactions by stating that for the process to move to the right removal of dissolved components is necessary. Others do not call attention to this very important factor. Actually, in layers of rock, stagnant groundwater occurs in contact with aluminosilicates for many millions of years, but gibbsite is not formed there. For the formation of this mineral prolonged flushing of the aluminosilicate rocks by weakly mineralized silica-free or low-silica warm rainwater is necessary, with removal of silica, alkalies, and alkaline earths. Under such conditions, we may represent the reaction of percolating hydrolysis by means of the following scheme:



In the brackets we have shown percolating water and the components dissolved in it; the arrow in front of the brackets represents influx of water, that after the brackets represents removal of the water with dissolved components in accord with progress of the reaction. The amount of percolating water n is a variable depending on the resistance of the aluminosilicate to decomposition, on the amount of silica subject to solution and removal, on the content of dissolved silica and carbon dioxide in the incoming water, on the temperature and pH, and on other factors. As a first approximation, on the basis of equilibrium of aluminosilicates with gibbsite, according to Garrels and Christ (1968) and Tardy (1969), and also from the data of Pedro (1971) on experimental weathering and Shvartsev (1976) on the chemical composition of lateritic water, we conclude that the value of n is very large, on the order of 200,000–500,000 units per unit of aluminosilicate. The water in the indicated scheme, although it passes from the left side to the right seemingly without change, is not passive. In thermodynamic calculations it cannot be abbreviated as in a mathematical equation. It decomposes albite and removes the dissolved components. It is precisely because of the removal of these components that the decomposition of albite takes place. Minerals of low stability, such as nepheline, are decomposed with the formation of gibbsite in temperate and even cold climates.

For an accurate representation of the cited reaction scheme of percolating hydrolysis we do not yet have unambiguous data. It needs further improvement. But, even in its present form, the scheme has fundamental importance: specifically, for hydrolysis of aluminosilicate with the formation of gibbsite or kaolinite in nature a tremendous amount of fresh warm rain-water is necessary. Laboratory experiments on the decomposition of aluminosilicates, set up by Pedro (1971) with consideration of this factor, have given positive results. Other investigators, endeavoring to decompose feldspars without percolating water, have attained no success.

In nature, one may frequently observe traces of the reverse reaction — the replacement of gibbsite, boehmite, or diaspore by kaolinite — the so-called silication or kaolinitization of bauxite. For this to occur, a high concentration of silica in the percolating water is necessary, on the order of 20–30 mg/liter, possibly more. At the Cheremushkino deposit, nests of bauxite have been found, replaced by montmorillonite; but this phenomenon is very rare.

Rocks and ores of the chemical weathering crust are distinctive metasomatic formations in which framework aluminosilicates have been replaced by kaolinite, gibbsite, or other minerals. From the geochemical point of view, however, it is found that during their formation the oxides of potassium, sodium, calcium, magnesium, and silicon have been replaced by hydroxides. The components of kaolinite or bauxite were already present in the rock. This process may be called hydroxyl metasomatism or hydrometasomatism, and the rocks may be called hydrometasomatites. This process commonly culminates with the introduction of bauxite components by descending or lateral currents of water.

Rocks of the chemical weathering crust — kaolin, laterite, bauxite, and others — in their degree of alteration of the parent rock are in no way outstripped by profoundly metamorphosed rocks, but the term "metamorphism" is used in geology to refer only to endogenic processes.

Reactions in the Laterization Environment

Physicochemical calculations of the stability of minerals in the weathering environment, made by different authors without consideration of percolating hydrolysis, do not correspond to observations in nature. Thus, Ginzburg (1963) wrote that feldspars and nepheline in a neutral environment are not converted spontaneously into mica, or kaolinite, or gibbsite, that energy from outside is required for this to occur. Such energy in tropical and subtropical countries is solar radiation in the opinion of that writer. But external energy is greater in hot springs with nearly neutral reaction than in the tropics, and gibbsite does not form in them. The error of Ginzburg lies in the fact that he did not consider the necessity of removing the silica and other soluble components.

Another example from the same author: "Little water is required for the formation of mica; 2.5 times as much is needed for the formation of kaolinite, and still more for gibbsite. It is therefore understandable that thick deposits of kaolinite and gibbsite, other conditions being the same, are formed in the presence of large quantities of moisture, i.e., in the subtropics and tropics;... consequently the decomposition of kaolinite to gibbsite is

possible only at low latitudes, in a strongly acid environment" (Ginzburg, 1963, p. 117). But in lakes, seas, and the oceans there is still more water, with no formation of gibbsite. It is true that the water of the oceans and seas is slightly alkaline, in most lakes nearly neutral. The statement of Ginzburg concerning the necessity of a strongly acid environment for the formation of gibbsite is inaccurate: the pH for formation of gibbsitic laterites is 5-7 according to many determinations; i.e., it lies in nearly neutral and weakly acid environments. Ginzburg's chief error is that he does not consider percolating hydrolysis in this case, the necessary removal of the dissolved components, a situation essential for the decomposition of aluminosilicates by warm silica-free water.

Tenyakov (1975), like many other geologists, quite properly believes that water and the conditions of its percolation through altering rocks are the principal factors of laterization. But in regard to the reactions of the environment, he takes the opposite position to that of Ginzburg: "In accord with numerous data... in the zone of most intense decomposition of aluminosilicate rocks the pH is not acidic but is always neutral or alkaline (7.0-9.0)" (Tenyakov, 1975, p. 9). Further he states: "The entire process of hydrolytic decomposition of K-, Na-, Ca-, and Mg-bearing rocks and the formation of a lateritic "structured" weathering crust takes place in an alkaline environment (pH 9.0-7.5), as predicted by theoretical considerations" (Tenyakov, 1975, p. 21). Laterization of kaolinitic clays takes place, in Tenyakov's opinion, through a wide range of pH, from 9.5 to 3.5, possibly even lower. This is too wide a range of alkaline-acidic indices for the medium of laterization; it is not supported in nature or in experiment.

Similar ideas were expressed by Bronevoi and his co-workers (1975). In noting the well-known data that in pellicular solutions surrounding grains of aluminosilicate minerals the pH reaches 7.6-9.6, these authors conclude that all conditions for the formation of pseudomorphous gibbsite exist here. These same authors indicate that the formation of bauxite "was allowed" also in weakly acid solutions. The zone of lithomarge in Western Africa, in the opinion of these writers, was formed after the bauxite zone, under cover of the latter. Unfortunately, strict proofs of the boundaries of the environment of bauxitization and the time of formation of the lithomarge are not cited. In the experiments of Pedro (1971) only the first part of the leaching of basalt by water took place at a pH of 9.0-9.5. Whether gibbsite or boehmite formed in this environment is not known. Further leaching with the formation of aluminum hydroxides took place at much lower pH, on the order of 7.3-8.0. However, even these values need refinement relative to stricter relations between the water being removed and the sites of basalt decomposition with the formation of gibbsite or boehmite. A weakly acid environment, on the order of 4.5-6.5, has been determined by many workers in waters of laterite blankets (Shvartsev, 1976; Bushinskii, 1971, 1975).

The extreme position in this matter is taken by Shcherbina. In her views, alkaline arid weathering leads to the formation of laterites, which are characterized by the presence of free Fe^{3+} and Al hydroxides. This position is in complete disagreement with the observations in nature, already noted previously (Bushinskii, 1975).

As may be seen, the basic error in theoretical discussions and statements of the earlier-mentioned writers relative to the necessity of an alkaline environment for decomposition of aluminosilicates and the formation of lateritic bauxites lies in the fact that they conclude without giving attention to percolating hydrolysis. A weakly alkaline environment arises readily in fracture water of intrusive and extrusive rocks, favoring the removal of K, Na, Ca, and Mg in aqueous solution. But such alkaline water is either stagnant or but faintly percolating. Decomposition of aluminosilicates therefore does not take place, does not lead to the formation of bauxite. Furthermore, silica and other components that have gone into solution do not promote the decomposition of aluminosilicates but rather foster their resistance, as widely observed in nature.

Current Diagenesis

Different types of diagenesis and their physicochemical essence have been investigated by Strakhov (1960). Sufficient data have now accumulated to permit us to distinguish a new type of diagenesis, which we call current diagenesis.

This type of diagenesis takes place on the bed of streams and through-flowing swamps, small lakes, and lagoons. The essence of the process is that mobile decomposition products of the sediment diffuse in all directions, find free egress to the zones where concentration

of the substance declines, in the present case to bottom water of low mineralization, are carried along by flowing water, and are removed beyond the basin. Iron and, to a less extent, silica are energetically removed in this process. Although the process is of great significance in the formation of white bauxites and refractory clays, already described long ago and amplified by later supplementary description (Bushinskii, 1956, 1975), further study is nevertheless necessary.

Free ferric oxides, introduced into the basin as goethite and hematite, settle and, in the sediment, are then subjected to the effects of decay products of organic matter. As a result, chemically immobile ferric oxide is reduced to mobile ferrous oxide, which is dissolved, diffuses to the bottom water, and is removed by this water. In this process the initially red ferruginous sediment is converted to low-iron rose color, rose-yellow, or white. This bleaching takes place not only with fine particles but also with initially red sands and pebbles of bauxite. Bleached bauxitic pebbles are the most important criterion of current diagenesis (Bushinskii, 1956, 1975).

Silica in the form of quartz and associated silicates is dissolved in the warm interstitial water and, like iron, diffuses upward into the bottom flowing water and is removed by it. Traces of this process may be seen in corrosion of quartz grains and locally in replacement of these grains by clay or gibbsite and replacement of feldspar and mica by kaolinite, which in turn is sometimes replaced by aluminum hydroxides.

A similar process of quartz corrosion and decomposition of silicates takes place also during lateritic weathering. The criteria for distinguishing flow diagenesis from lateritization are chiefly geological. They are clearly distinguished in recent rocks in which vertical percolation may be observed directly in nature. The matter is much more complex when studying fossil sediments, especially where flooding and lateritization have alternated in the same zone because of seasons of rain and desiccation. Such complex variations apparently took place during formation of the Arkalykskoe bauxite deposit of near-karst type in Kazakhstan (Tsekhovskii, 1976).

Distinctive features of current diagenesis of bauxites and clays are white color or low iron content, presence of carbonaceous substance ($C_{org} > 0.5\%$), and, in places, impermeable layers beneath white clays or bauxite, making downward percolation of water difficult.

Depending on the composition of the initial material, the extent of through-flow of the basin, the content and quality of organic matter in the sediment, the rate of sediment accumulation and the seasonal character of flooding, and the chemical composition and temperature of the water, different products of current diagenesis are formed. Let us consider some examples.

Bauxite deposits of the Tikhvin bauxite region occur at the heads of ravines of Viséan age (Early Carboniferous). At the very head of a ravine the bauxite is red, with pebbles of bauxite. Downward along the ravine the bauxite and pebbles become rose-colored, less ferruginous. Lower they become grayish white, and still farther they grade into kaolinitic bauxitic clay, which gives way to kaolinitic clay and then kaolinitic-hydromicaceous clay. These clays are grayish white or gray from admixtures of organic matter. The color of the bauxite pebbles is red in the red bauxite, rose-colored in the rose bauxite, and grayish white in the grayish white bauxite. Within some dense pebbles, red or rose-colored material has been preserved (Bushinskii, 1975).

These facies changes from the head of a ravine downward along the course of the stream may be considered diagenetic or facies-diagenetic. The bauxite pebbles and bauxite and clay particles brought into the ravine were initially red because of admixtures of goethite and hematite. Deposited in the upper dry part of the ravine (the near facies zone), they have remained red. Downward, in the zone of intermittent flooding of the ravine (the middle facies zone), the bauxitic material was deposited together with plant remains. Traces of these remains have been preserved in the form of prints of vertical stigmarian roots. During decomposition of plant material, ferric oxide was reduced to ferrous in the sediment and removed. As a result, the initially red bauxite was converted to low-iron, rose-colored material.

An analogous process of iron removal took place in the zone of constant flooding (the far facies zone), but more intensely. The principal proof of iron removal in diagenesis is the fingerlike wedgeout of red bauxite downward in the landscape toward light bauxitic and bauxite-free clays, and also the different colors of the bauxite pebbles. Changes in the color of these pebbles could not be due to mechanical sorting in accord with color. We must

assume that bleaching of the bauxite pebbles took place as a result of removal of iron during current diagenesis.

Current diagenesis was accompanied by the removal of silica as well as iron from the sediment. The example of the Tikhvin deposit as demonstrating removal of silica is not very convincing, since the bauxite here is very fine. One may frequently observe split leaves of mica (whisks), replaced by hydromica, and, on the ends of the whisks, kaolinite.

Removal of silica may be clearly seen in the white quartzose sandy bauxites of the Ukraine. These bauxites also occur in ancient stream valleys, but the valleys are not cut into clays, as at Tikhvin; they are cut into a granite massif. The age of the bauxites is Early Cretaceous: Aptian-Albian. In thin sections of these bauxites, one may clearly see numerous quartz grains, which are strongly corroded and completely or partly replaced by gibbsite. The sedimentary character of the bauxites is demonstrated by their interlayering with lenses of quartz sand, refractory clays, and lignite. The replacement of quartz by gibbsite and the removal of silica are explained by current diagenesis. Such replacement has been observed by many investigators also in Cretaceous-Paleogene bauxites of the Urals, Kazakhstan, and Siberia. It is now difficult to explain this everywhere in the same way, since recently several laterite horizons with distinct bauxitization of clays have been identified by Tsekhovskii (1976) at the Arkalykskoe deposit in Kazakhstan.

The large and rich deposits of low-iron bauxites on the northern submerged part of the Guiana shield of South America are also good examples of current diagenesis. "More or less complete solution of quartz grains and partial replacement of the grains by gibbsite are very widespread in the bauxite deposits of Surinam (formerly Dutch Guiana) and Demerara (Guyana, formerly British Guiana), both in lateritic deposits and in deposits occurring with sedimentary kaolinitic clays (Van Kersen, 1956). Judging from Van Kersen's description, the bauxite deposits of the latter type, among the largest and best sorted in the world, were apparently formed by diagenetic replacement of quartz and kaolinite by gibbsite and by the removal of iron and silica in a through-flowing swamp" (Bushinskii, 1958, p. 438). This idea was discussed in more detail at a later date (Bushinskii, 1971).

Support of this idea may be found in recent observations by Valetton (1973, 1974) in the provinces of Mungo and Onverdacht in Surinam. This investigator has noted that the parent rocks for formation of the Onverdacht bauxite deposits were poorly sorted red sediments: kaolinitic clays and kaolinitic quartz sandstones. The material of these rocks was brought in by fast turbidity currents from the adjacent highlands. In the lower parts of the section, bedded clays and sandstones with layers of heavy minerals have been preserved. Above, in the bauxite layer, these rocks are but rarely encountered, as relicts. It is Valetton's conclusion that in the early stage of diagenesis ferruginous minerals, kaolinite, and quartz were destroyed. In the process silica was removed, but alumina was precipitated here in the form of gibbsite. The dimensions of gibbsite crystals or grains at the base of the layer are rather large, but at the top they are very small. Iron migrated in part or was precipitated in hematite concretions within the active groundwater layer. These processes explain the high porosity and brecciaform appearance of the gray bauxites. During epigenesis further mobilization of iron and aluminum took place, precipitation of these elements in pores, and kaolinization of bauxite because of the introduction of silica. As may be seen, Valetton, though she was not acquainted with my work, came to similar conclusions.

The far zone of current diagenesis has been studied in lowland peat bogs of the Kolkhida lowland in the Caucasus (Timofeev and Bogolyubova, 1972; Timofeev et al., 1974). The sources of discharge were 40 km and more from these peat bogs. The investigators studied more than 50 sections of peat deposits; from the content of humified plant material, the degree of its decomposition, and the composition of the phytocoenoses, they distinguished 17 genetic types of sediments. Fine fractions of sand-silt sediments from the Rioni channel and other streams are made up of hydromica, kaolinite, montmorillonite, and chlorite. These minerals are believed to be primary by the writers. A clay-humus facies of sediments with a pH of the water of 4.0-5.5 has been distinguished in the genetic group of woody peat bog deposits. These sediments are gelinitic-precollinitic woody peat, strongly humified, with a content of 40-65% organic matter and 60-35% mineral substance. In thin section, the clay part of the peat is indeterminate for the most part, but where there is comparatively little of it, it is brown, colloform, with undulatory extinction. Authigenic amorphous silica has been noted, filling cellular cavities in wood tissue. In the clay fraction <0.001 mm of the sediment, the ash content was determined chemically - 22.04% - and the following components were identi-

fied in the ash: 56.44% SiO₂, 1.42% TiO₂, 24.04% Al₂O₃, 4.09% Fe₂O₃, 0.03% MnO, 9.57% CaO, 0.50% MgO, 1.24% Na₂O, 2.23% K₂O, and 0.43% P₂O₅; a total of 99.99%. The ash was found to contain 5.29% amorphous SiO₂ and 4.34% free Al₂O₃. This unnatural association of free silicon and aluminum oxides and the high CaO content require study.

With increase in the content of organic matter, on going from lacustrine-alluvial clays to clayey and purer peats, the following changes are observed in the content and transformation of clay minerals. The montmorillonite content declines up to disappearance, but kaolinite increases. In this progression the interplanar spacing in montmorillonite increases to 19 Å (with saturation of the sample with glycerin). The writers explain this by adsorption of molecules of organic compounds on basal plane surfaces. Destruction of the crystal lattice of montmorillonite in swamps takes place immediately and is accompanied by the appearance of allophane and kaolinite. The kaolinite here forms from the decomposition products of montmorillonite synthetically, and is not the course of gradual transformation of this mineral.

In chlorite, with increase in content of reactive organic matter in the sediment, the number of vermiculite layers increases until the mineral is converted to vermiculite. However, one may find chlorite that is stable in peat bogs, insoluble in 10% HCl. Low-iron chlorite are normally stable, but in the given case it was not possible to separate them for investigation.

The destruction of montmorillonite and the transformation of chlorite are accompanied by reduction of iron content in the clay fraction, from 8-12 to 4-5%, and a reduction of magnesium from 4-5 to 0.5% occurring in the clay minerals. Destruction of hydromica because of reeds that grow in the bog is interesting. This relation may be seen from the fact that 20-27% K₂O was measured in ash of the reed, but only 6-9% in ash of alder. The remaining semi-destroyed hydromica is easily dissolved in 10% HCl.

Thus, the authors have found that change in the composition of clays in a number of sediments depends on the silt-clay to peat bog facies. Whereas lacustrine clay is represented by kaolinite, hydromica, montmorillonite, and chlorite, the clay part of woody peat in the same section consists of kaolinite, hydromica, and vermiculite, and the clay part of reed peat consists chiefly of kaolinite and vermiculite. The role of facies is definite and controlling in the transformation process of clay minerals, but the reactivity of organic matter accelerates the process.

In waters of the Chernaya (Black) and Amtkel karst rivers in the Main Caucasus, and also in the ephemeral lake on the flood plain of Rioni River, Zverev and Timofeev (1975) have noted low contents of H₄SiO₄ - 3.0-5.6 mg/liter - at a pH of 7.6-8.95 and a total mineralization of 150-226 mg/liter. These investigators calculated the corrosiveness of lacustrine, stream, and swamp waters of Kolkhida in Georgia and prepared diagrams showing the equilibrium of gibbsite with albite, microcline, anorthite, kaolinite, chlorite, and montmorillonite. On the basis of these data they prepared a map of Kolkhida with designation of vast areas of hydrolytic decomposition of aluminosilicates with the formation of gibbsite in channels and on flood plains of streams. The processes of percolating hydrolysis and current diagenesis in this region requires further investigation.

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UDC 551.31

A detailed study of soils of Carboniferous age in the Donets basin has shown that they have a differentiated profile with well-defined upper (eluvial-accumulative) and lower-lying (illuvial) horizons, which may be identical with horizons A and B of modern soils. The soils of the productive suites of the Middle Carboniferous are distinguished from soils in the nonproductive suites in the Lower, and especially the Upper, Carboniferous by their thickness, color, and the structure of individual horizons, as well as by the nature and degree of decomposition of plant material, the shape and structure of concentric soil concretions, by the intensity and trend of compositional changes in the clay fraction, and by other indices. The soils of the productive suites are also heterogeneous. Several types are distinguished in them which are limited to different elements of the landscapes of a near-sea alluvial plain: the interfluvium of a dissected near-estuary river valley, areas more distant from the estuary, the central part of the valley, and the reservoir.

In the past decade, interest has noticeably increased both here and abroad, in the study of fossil soils. The formation, in 1965, of a special international commission in INQA has contributed to this, which is conducting a systematic study of soils of the Quaternary period. Bibliographic-information collections prepared by it number several hundred works devoted primarily to the study of buried soils. In 1974, a collection in monograph form appeared (Paleopedology, 1974), published by the Academy of Sciences of the USSR and a general study of paleosoils in loess deposits of the Recent in Ukraine territory. The problems which are held by the authors of similar studies to be decisive to one degree or another in soils of the Quaternary period are wide-ranging and varied. Besides those of a peculiarly soil-science nature (the extent of notions of the origin of soils and their evolution with time), there are: the reconstruction of physical geographic conditions and ancient landscapes, including their biochemical features; the use of fossil soils for detailed stratification; the elucidation of sources and duration of pauses in sedimentation; the explanation of the role of soil-forming processes in the formation of continental deposits ("pedolites"); the study of fossil soils in connection with the confinement of mineral resources to them.

The science of ancient soils, paleopedology, thus goes far beyond the limits of soil science and is of primary interest to geologists, without whose participation it obviously cannot develop fruitfully. This especially refers to the ancient soils of Mesozoic-Paleozoic age, where there is the additional problem of "removing" later factors of the regional alteration of rocks and soils.

There is extremely little lithofacies research, including the special study of ancient soils; we have mainly the works of V. I. Chalyshev (1974) on Permian soils. Carboniferous soils have been studied in connection with bauxites in the U.S.A. (undercoal soils, known by the name of "underclay").

The present article is itself a brief generalization of the results of Carboniferous soil studies in the Donets basin along with B. P. Gradusov (Dokuchaev Soil Institute) and L. G. Rekshinskaya (Moscow State University). Detailed data is published in a number of works (Feofilova, 1971, 1972, 1975; Feofilova and Rekshinskaya, 1973; Feofilova and Gradusov, 1975).

Institute of Geology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 44-50, November-December, 1977. Original article submitted February 2, 1977.

The soils were studied from a fresh well core and in pit mines within the southwestern part of the Donetsk basin, in regions of low coal-metamorphism. Micromorphological (study under the microscope), electron microscopy, x-ray, and chemical methods were used.

Soils of the Middle Carboniferous Productive Suites

These were studied mainly in the suites C_2^5 and C_2^4 , below the coal seams. These are altered zones 0.5-2 m thick, which are gradually transitional toward the bottom into normal sedimentary rocks. The structure is distinctly bipartite. The upper horizon, darker and more argillaceous, nonstratified, with a nodular texture and frequent surfaces containing abundant, unordered root remnants (stigmata with appendices) is known by the designation "curly." In the upper part of it, a clay subhorizon is sometimes distinguished, saturated with horizontally layered plant remnants, very similar to the forest bedding of modern soils. The lower-lying horizon, lighter and more compact, nonstratified or with relics of destroyed primary sedimentary stratification, contains vertical root fragments and carbonate concretions of siderite or ankerite-siderite composition. They are most often distinguished by a root or irregular nodular shape with a finely hummocky surface. The soils are colored a gray tone, differing slightly or not at all from the color of the surrounding rock.

Microscopic study reveals the following features of the horizon. In a direction away from the rock (primarily siltstone), and toward the upper part of the soil, progressive destruction of the clastic material is observed: sericitization of the feldspars, hydration of the micas, corrosion of the quartz grains and as a result, an increase in the clay cement. Toward the top, there are usually no more than 15-20% clastic grains, and they preserve their size from the original rock, differing only in having worse sorting. The sharp disruption here of the ratio between the amount of cement and the size of clastic grains relative to the unaltered rock is evidence in favor of the soil nature of argillization, which, naturally, does not include the original heterogeneity of the rock in a number of cases.

Root fragments are more or less intensely gelled, but in the upper horizon completely opaque ones are also encountered, with clear outlines and which splinter easily, with the formation of detritus and dust. Their nature may be conditionally associated with the process of fuseinization. Pyrite is usually developed along plant fragments, the content of which is closely associated in the upper part of the soil with the facies character of the roof of the coal mass: the more marine the roof, the more pyrite.

In the dispersed clay, optically oriented clays (OOC's) are widely developed, both wavy and felted types, with orientation of the partings along the root fragments. In some soils, a brown colloform (marker) clay is encountered, pigmented with organic gel, which confirms a certain mobility of organic mineral colloids.

Carbonate material in the upper horizon is, as a rule, lacking, while in the lower it is encountered almost exclusively in concretionary form with the widespread participation of spherulites agglutinating into aggregates.

The mineral composition of the clay fraction of the soils and original rocks is qualitatively similar. Hydromicas and kaolinite predominate; a mixed-layer mineral (mica-montmorillonite) and an insignificant amount of chlorite are present in lesser amounts. However, in relation to quantity, changes in a direction away from the original rock toward the upper part of the soil are sometimes very substantial and not always uniform. Most often, a decrease in chlorite content and an increase in kaolinite are observed. In order to make precise the quantitative changes in the content of individual minerals, the method of "probable evaluations" was used (Feofilova and Gradusov, 1975), with which there could be successfully distinguished, in particular, the primary sedimentary enrichment in kaolinite in the upper part of certain soils from later enrichment conditioned by soil-forming processes. For this purpose, the chemical analyses of the soils and rocks were recalculated for the nonquartz portion and corrected with a change in weight by volume. In addition, the corrected oxides were recalculated (relative to the original rock), based on "variable groups of oxide-indicators" (Feofilova, 1975). Data worked out in a similar way for the chemical analysis have shown that in the upper horizon of all the soils, C_{org} content and pyritic iron are increased, FeO , CaO , MgO , and Na_2O are decreased, and K_2O is also decreased in the majority of cases, while the first three oxides form a maximum within the lower horizon which coincides with a CO_2 maximum. The SiO_2/Al_2O_3 ratio either does not change or decreases toward the top of the soil; this occurs due to both a decrease in SiO_2 as well as accumulation of Al_2O_3 .

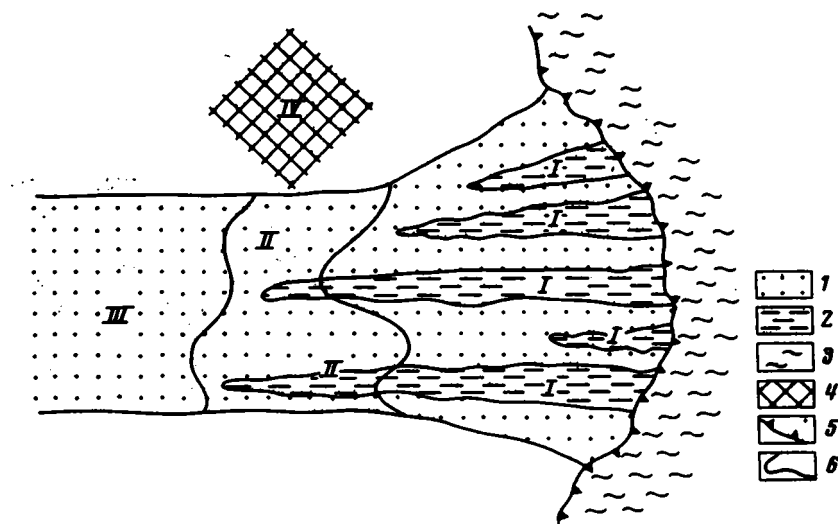


Fig. 1. Sketch of zonal distribution of fossil soil types in a near-marine river-valley landscape. Facies (1-3): 1) channel, 2) tidal-marsh-lake (interchannel areas), 3) deltaic and near-shore marine; 4) watershed area; 5) position of sea shoreline. 6) Boundaries of zones I-III (explanation in text).

The data presented permit the identification of the upper and lower horizons of Carboniferous soils relative to the accumulative-eluvial horizon A and illuvial B of modern soils and the confirmation of the presence of ancient soil profiles which have preserved many features which are determined by the soil-forming processes of this time. Looking at the details of the structure and composition of the soils against a background of paleogeographic maps for the end of the regressive phase of each sedimentary cycle, i.e., for the time immediately preceded by soil formation (Zhemchuzhnikov et al., 1960) has permitted the separation of four groups of soils, the distinguishing features of which are detailed by the elements of the landscape and microclimate (Fig. 1).

I. Soils located in the near-estuary part of river valleys, between individual branches and streams, near the shoreline of a marine basin, has a dark gray horizon A, 35 cm average thickness, often with a subhorizon A₀ (forest bedding). Root fragments are primarily gelled, but there is hardly any organic gel which is not associated with fragments. Horizon B has an average thickness of 70 cm, a gray color, structure primarily stratified, and degree of root-fragment decomposition even slighter. Carbonate material is contained in disseminated form and only occasionally agglutinates around root fragments; its composition is purely sideritic, no spherulites are encountered. Traces of clay matter transformation are absent. On x-ray-grams, distinct reflections of hydromica and kaolinite are established, a mixed-layer phase is hardly expressed at all, and there is no chlorite. There are either no changes along the soil profile, or else they are determined by the sedimentary heterogeneity of the rock.

All these indices are in accordance with the lowland position of these soils which have developed under conditions of long-term water-logging and slight drainage under hygrophilous vegetation. It may be supposed that the basic process which controlled the formation of these soils is gleying. A green (dove-colored) color, which is characteristic for modern gley soils, is here masked by poorly decomposed plant fragments, a hydromorphous coarse humus of black color with large molecules (DuChauffure, 1970). The absence of a spotted horizon with deposits of iron hydroxide is probably associated with secondary (in relation to the soil) regional gleying of the soils and rocks in a reducing medium in aquifer horizons, which is also noted for Recent soils of the Ukraine (Sirenko, 1974).

II. Soils located within a dissected river valley at a greater distance from the shoreline have a somewhat thicker horizon A (average 50 cm). Its coloring is distinguished by a slight brownish tinge; the subhorizon A₀ is absent. Opaque fragments are encountered more often, and at the same time a brown organic gel is present here, which has lost any obvious

association with plant fragments; it saturates the clay, with a tendency toward the formation of small aggregates. Along with the indices of flocculation in organic mineral colloids, their mobility is quite clearly expressed: they form rims around siderite spherulites and in horizon B colloform (marker) inclusions.

A slight greenish tinge appears in the coloring of horizon B. Root fragments are poorly distinguishable by means of the naked eye; under the microscope, it is evident that they are replaced by carbonate and more rarely by OOC. Carbonate is represented by spherulites of siderite which flow into microaggregates; occasionally they form rims which developed on spherulites only at the top of this horizon.

To this group of soils there is confined an intense soil kaolinization which is accompanied by destruction of the hydromica and chlorite. Here a very energetic transport from horizon A is established for alkalies, alkaline earths, and iron. Distinctive features of the given group confirms the improvement of drainage and the periodic drying of the soil, which contributed to a more intense humification of the plant material. Based on all these indices, we have here the matter of the process of gley kaolinization (Perel'man, 1968), which occurs under conditions of an acidic medium of a reducing order.

III. Soils located within an undissected river valley, at a significant distance from the shoreline. In these soils further enhancement is found in the process of mineralization and humification of the plant fragments. The aggregate structure of horizon A appears more clearly (flocculation, with the formation of clay-humus clumps), at the same time as the mobility of organic mineral colloids is noticeably decreased: rims are not formed and colloform clay is rarely encountered. Carbonate in horizon B is represented only by siderite spherulites and their aggregates, which attain the size of macroconcretions. Carbonate and pyrite are highly oxidized. From bottom to top along the profile, the content of hydromica decreases and that of a mixed-layer mineral with a tendency toward ordering increases. The intense removal of iron is established, as well as the relatively reduced removal of alkaline earths. An increase in the oxidation-reduction potential (and possibly pH) was apparently the main reason for the cessation of soil kaolinization.

IV. Soils located outside the river valley (in the watershed) were studied below the k_0 coal seam, which splits after a short distance (2-3 km) into two: k_0^l (working) and k_0^u (thin or absent). The soils are distinguished by a small thickness (40-60 cm), slight differentiation in the horizons, and generally preserved bedding. The color is gray to dark gray. Plant fragments are opaque, slightly broken up into dust, scattered among the clots of brown gel which sometimes form brown clumps 3-4 μ in diameter. There are no macroconcretions; the amount of carbonate material is generally low. The soils are also distinguished by an increased content in Fe_2O_3 and iron pyrite and by insignificant changes in other oxides along the profile. In the clay fraction of the original rock, kaolinite predominates, but in the soil the amount of it decreases, again increasing at the highest horizon A_0 , which finds expression in chemical analysis data. The mixed-layer mineral changes quantitatively in inverse proportion to kaolinite; this brings to mind the notion of a closed system with a predominance of an automorphous phase in the development of these soils. It is also possible to note the effect of topography. The thickness of the soil is 20 cm in all in the elevated areas (unfoliated seam), horizon A is apparently partially eroded, the horizon B is incompletely developed; carbonate material is completely absent. In the clay fraction of the soil, the content of the mixed-layer mineral is strongly increased with a large amount of montmorillonitic groups and an unordered type of layering. In the direction of the splitting of seam k_0 , the thickness of the soil below k_0^l increases reaching a normal average in the area where the distance between k_0^l and k_0^u is equal to 20 m (the central part of the local depression). At the same time as this, the role of gelled plant fragments is somewhat increased here, carbonate material appears below, and a mixed-layer phase acquires features of ordering.

On the whole, the soil here displays features of insufficient maturity and of partial erosion locally, and the formation under conditions of elevated Eh of weak hydromorphism as well.

Soils in the Nonproductive Suites of the Upper and Lower Carboniferous

The soils of the nonproductive suites have been studied by individual sections. As a result of this, and also thanks to the absence of paleogeographic maps, we shall set down here only certain general features of these soils, which distinguish them from those considered above and which reflect regional changes in landscapes and climate conditions.

With the Lower Carboniferous, the most specific soils are in the $C_1^4(D)$ suite of the Namurian stage. On the whole, they are similar to the soils of group 3 from the productive suites. Externally, they are distinguished by a great thickness in horizon A (60-cm average) of friable composition, with a well-expressed fine-nodule structure. During weathering, the soil crumbles into fine aggregates of clastic grains, cemented by humified clay. Plant fragments are undifferentiable.

Study under the microscope indicates about the same character and degree of decomposition in plant material as in group 3, but humus is less mobile and only sometimes (soil under a thin coal seam) forms double or even triple rims around carbonate spherulites. Mobile forms of OOC are also very slightly expressed.

In an obvious connection with this, the fact comes up that carbonate material in the form of spherulites is encountered along the entire profile, only enriching horizon B, relatively speaking. Here the spherulites do run together into aggregates, but form botryoidal accumulations along thin branching radicles. These areas create the impression that the spherulites fill up the cells in the plant tissue. Their composition is sideritic with spots of ankerite and is locally pure ankerite. The clay fraction is distinguished by an increased content of chlorite and decreased kaolinite with a sharp predominance of hydromica. Upward along the profile, hydromica and chlorite are transformed into a mixed-layer phase of complex composition. Chemical analyses indicate a substantial increase in Fe_2O_3 (with a maximum in horizon A up to 5%), removal of FeO , and insignificant removal of alkalies and alkaline earths, while CaO and K_2O sometimes even increase in the upper part of horizon A. Compared to the productive suites, the soils considered were formed under temporary humid climatic conditions with even more frequent periods of drying out and apparently under some other, nonhygrophilous vegetation.

Within the Upper Carboniferous, the sedimentation conditions change toward progressive dryness with simultaneous lessening of the mobility of the Donets downwarp, due to which there occurred not only the gradual disappearance of its coal-bearing nature, but also essential changes in the character of the landscapes (Feofilova, 1966). The clearest reflection of these changes is in soils from the uppermost suite C_3^2 . These soils are slightly cemented and varicolored, with an alternating predominance of now greenish (dove-colored), now brownish-red tones. Against a red background, the greenish spots are developed along decomposed root fragments, and against the green background the brownish-red root-shaped spots are caused by the content of organic gel with iron hydroxide. In the upper part of these soils, there are always abundant, fine, irregular-nodular concretions of a calcite-dolomite composition. Under the microscope, the widespread development of iron humates is evident, from dense, recrystallized spots forming microortshteins, lenses, and rims around grain aggregates to amorphous ones. Frequently in the center of an amorphous inclusion, relics of altered plant-tissue radicles are distinguished. Also present are fine, opaque fragments up to dust-sized. In the lower part of the soil, microdeposits of a carbonate of dolomite-ankerite composition are observed, interlayered along concentrates of organic matter (apparently of the altered radicle), toward which in the peripheral part an even larger amount of iron hydroxide is added. The composition of the clay fraction is distinguished by the widespread development of a mixed-layer phase of complex composition, with the presence of two types of interbedding, with different contents of montmorillonite groups (with reflections for 12.7 and 16.5 Å). Changes along the profile are insignificant. The content of iron hydroxide is increased in these soils to 7.5%, while C_{org} content falls to a trace or part of one percent. Pyritic iron is not established (all the pyrite is oxidized), and the leaching processes are attenuated.

One may conclude that formation of these soils proceeded under conditions of increased mineralization and humification of plant material with its subsequent conversion into an insoluble organic-iron form. A major factor was the elevation of Eh in connection with initial arid-climate formation. Nevertheless even under these conditions, the soils bear signs of temporary hydromorphism, even more so due to atmospheric precipitation. At the same time, the peculiar association of iron-oxide compounds, of the type of ironpan in modern soils, with calcite-dolomite concretions of the upper horizon are evidence of sharp variations even in groundwater level.

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REASONS FOR THE ANOMALOUSLY HIGH BORON CONTENT IN BAUXITES FROM CERTAIN DEPOSITS

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UDC 553.492.1:546.27

Against a background of overall, more or less uniform boron content in bauxites, from the majority of ore deposits (40-60 g/ton) in the Kursk Magnetic Anomaly (KMA), the Obukhov deposits in Salair, and the Vezhayu-Vorykvino deposits in central Timan, an anomalously high (more than 100 g/ton) concentration of this element was distinguished. In the KMA, such an anomaly is associated with boron impurities (tourmaline) in the primary rocks, Precambrian phyllites. The bauxites of the Obukhov and Vezhayu-Vorykvino deposits bear visible traces of the influence of postore hydrothermal-metasomatic activity, with which their enrichment in boron is also associated.

An analysis we presented relatively recently for the basic distribution patterns of boron in bauxites (Edlin and Tenyakov, 1975) showed in essence a picture of rather uniform distribution of this element both in bauxites of individual deposits and in their various lithostructural and lithofacies types. Only the bauxites of laterite covers (on the average) were noticeably distinguished by a lower average distribution of boron (15 g/ton), in comparison with sedimentary bauxites of platform (46 g/ton) and geosynclinal (55 g/ton) areas (also on the average).

However, as has been indicated in the study already mentioned, against a background of overall, more or less uniform boron content in bauxites in the majority of deposits, several of them were noticeably distinguished by an anomalously high content of this element. We consider an anomalously high boron content in bauxites to be one exceeding 100 g/ton, although not established in individual samples but in the deposit as a whole.

Up to the present time, three deposits have been distinguished with similarly clearly elevated contents of boron. These are the KMA bauxites (Kurenkina, 1973; Edlin and Tenyakov, 1975; Varik and Parshakov, 1975), the Vezhayu-Vorykvino (central Timan) deposits, and the essentially corundum ores of the Obukhov deposit (Salair ridge) (Table 1).

For comparison in Table 1, the average contents of boron are presented for a typical platform (Arkalyk) and typical geosynclinal deposit (Northern Ural Bauxite Mines), as well as for bauxites of the Berdsk-Maya deposit lying near the Obukhov, but not affected by the action of intrusion, which metamorphosed the ores of the Obukhov deposit.

One must mention that only for the KMA bauxites has the opinion been expressed that the elevated boron content in the bauxites of this deposit is associated with the presence in the original rocks of noticeable amounts of tourmaline.

We will look in more detail at the distribution patterns for boron in bauxites and other rocks which participate in the geologic makeup of the regions of these deposits.

As is well known, the basic mass of bauxites and bauxitic rocks of the KMA is limited to the upper part of the profile of the laterite weathering crust, which formed in Lower Carboniferous time along sericitic and chloritic phyllites of the Kursk metamorphic series in the Lower Proterozoic. The thickness of the weathering crust in the phyllites measures from 30 to 70 m. Its complete profile consists of the following zones (from bottom to top):

slightly altered phyllites;

primary development of hydromica minerals;

All-Union Scientific-Research Institute of Mineral Raw Materials, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 51-59, November-December, 1977. Original article submitted August 4, 1976.

TABLE 1. Boron Content in Bauxites of Several Deposits in the USSR

Deposit (region)	No. of samples	B, g/ton			Wt. %		
		from	to	av.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
KMA (center of European USSR)	14	1300	3200	2082	8,77	46,84	8,42
Vezhayu - Vorykvino (central Timan)	57	34	370	125	9,8	49,6	19,8
Obukhov (Salair)	23	19	1400	169	16,89	50,50	10,25
Northern Ural Bauxite	47	16	103	41	2,70	54,48	17,17
Mines (northern Urals)							
Arkalyk (central Kazakhstan)	36	16	95	44	5,01	50,01	14,21
Berdk - Maya (Salair)	14	12	100	27	12,12	51,05	5,74

TABLE 2. Boron Content in Bauxites and Enclosing Rocks of the Vislov Deposit, KMA

Rocks	No. of samples	B, g/ton*			Wt. %				
		from	to	av.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Σ Fe ₂ O ₃
Clay, carbonaceous with pyrite	1	—	—	1600	4,14	5,08	—	—	33,40
Shalelike chamosite rock with pyrite	1	—	—	1400	20,02	23,52	—	—	35,93
Bauxites, clastic	6	1300	1650	1430	7,36	41,75	16,82	13,46	31,76
Bauxites and alites, pseudomorphous	8	2000	3200	2800	11,42	51,57	4,78	14,42	20,78
Shales, kaolinite - hydromicaceous	8	1100	2700	1860	39,68	29,73	13,23	3,24	16,82
Shales, quartz - chlorite - sericitic	2	790	1100	950	67,36	16,56	3,58	0,58	4,22

*Analysis done by the atomic absorption method: sensitivity 0.005%, rel. error 10-20%.

kaolinite clays;

bauxitic rocks and bauxites.

In all cases, the transitions between the zones are gradual, but the formation of weathering products is pseudomorphous. In the zone of bauxite development, secondary processes of chamositization, sideritization, and calcitization are widely displayed. Occasionally, the development of the latter ones is accompanied by the noticeable removal of iron from the bauxites (bleaching) and by a certain redistribution of aluminum.

Based on mineral composition in the eluvial bauxites of the KMA, they were subdivided into the types boehmite (chamosite-boehmite, kaolinite-boehmite), gibbsite (chamosite-gibbsite, chamosite-boehmite-gibbsite, kaolinite-gibbsite), and the rather rare chamosite-hematite-boehmite.

In addition, within the limits of laterite-cover development in the KMA, clastic bauxites are also known, but they have subordinate significance.

The rocks of the weathering crust and the products of their redeposition are immediately overlain, with sharp angular unconformity, by sedimentary cover 400-600 m thick, at the base of which lie limestones and terrigenous, carbonaceous sand-clay deposits of the Lower Carboniferous.

Analysis of the data summed up in Table 2 indicates that in the KMA deposits, pseudomorphous bauxites are especially rich in boron; boron content in the clastic bauxites is two times lower. Let us turn our attention to the fact that the original rocks for the bauxites (quartz-sericite-chlorite shales) are characterized by an extremely variable amount of boron, which reflects just as variable a content of accessory tourmaline in them (A. P. Nikitina, oral communication). In the two samples of these shales which we studied, boron content is 950 g/ton, on the average.

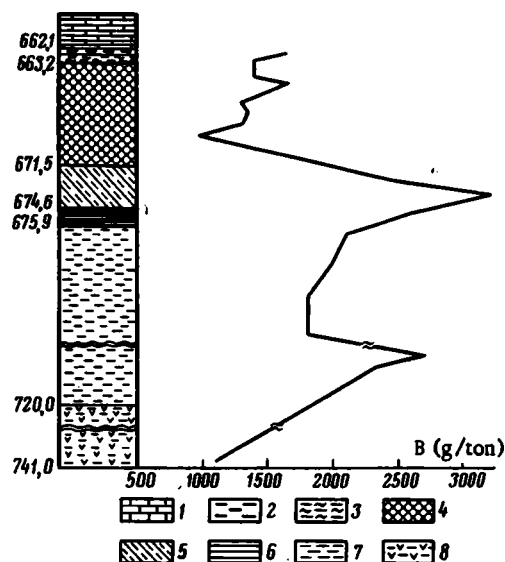


Fig. 1. Change in boron content in a section of the weathering crust in the Vislov deposit, KMA (hole 1780). 1) Limestones, 2) carbonaceous clay with pyrite, 3) shalelike chamosite rock, 4) clastic bauxites, 5) pseudomorphous bauxites, 6) pseudomorphous alites, 7) kaolinite-hydromica rocks, 8) phyllitelike rocks (original).

As one of the examples of the character of boron distribution in the ore-body section, we present data we obtained from hole 1780 (Vislov deposit) (Fig. 1). The very uneven distribution of the element studied in the weathering-crust section draws attention to itself. The fact that boron in the bauxites and enclosing rocks is concentrated mainly in tourmaline is graphically established by microscopic study of the bauxites and original phyllites. This is also indirectly confirmed by the earlier-mentioned factor of a decrease in boron content in redeposited bauxites and alites in comparison with their eluvial analogues, which takes place positively due to loss of part of the tourmaline during the sedimentary differentiation of matter.

It is interesting to note that widespread distribution of clastic tourmaline in Proterozoic metamorphic rocks is observed in many regions of the Russian Platform and the Ukrainian crystalline shield (Lapinskaya, 1963).

Passing to the bauxites of the Obukhov deposit on the Salair ridge, one must immediately turn one's attention to the fact that of all the limestones in this region of deposits and ore occurrences of Devonian age, this very deposit is distinguished by a very high degree of metamorphism in the rocks of the ore horizon, which is evoked by the influence of the near-lying Vydrikhov adamellite intrusion and numerous dikes of diorite, diorite-porphyry, granite, khersantite, and other rocks cutting the ore bodies. As a result of the processes of contact metamorphism, all the bauxites of the Obukhov deposit are transformed into essentially corundum-mica-leptochlorite rocks or varieties of them, composed primarily of any one of the minerals indicated.

Bauxites of the basal Lower Eifelian horizon lie with an erosional unconformity on light gray and gray, medium- and fine-grained reef limestones of the Khvoshchev suite in the Lower Devonian (Lower Emsian), forming a body of unexposed thickness (from 2-3 to 16 m). It is overlain by black pyritized shales of the Lower Eifelian. The underlying reef limestones in contact with the bauxites are intensely leached, crushed, and impregnated with bauxitic matter ("subore breccia").

In the ore horizon, bauxites of corundum and mica corundum with leptochlorite admixture are distinguished. Among the latter, alites are encountered which are not visually dis-

TABLE 3. Boron Content in Bauxites and Enclosing Rocks of the Obukhov and Berdsk-Maya Deposits (Salair ridge)

Rocks	No. of sam- ples	B, g/ton			Wt. %			
		from	to	av.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO
Obukhov deposit								
Limestone, dark gray (roof of the ore body)	2	6	22	14	3,65	2,85	0,27	0,20
Bauxites, corundum and micaceous - corundum	23	19	1400	169	16,89	50,5	10,25	6,68
Alite, corundum - micaceous	13	14	3500	605	24,90	41,74	6,23	7,82
Khersantite (from dikes)	1	—	—	23	68,40	15,10	1,80	0,97
Granite porphyry (from dikes)	1	—	—	16	69,00	15,00	1,43	1,44
Limestone, light gray (base of ore body)	1	—	—	8	0,55	0,50	0,73	0,07
Berdsk - Maya deposit								
Bauxites, dark gray, leptochlorite - diasporitic	10	12	39	20	7,69	54,06	7,30	8,44
Bauxites, gray, chlo- ritoid - diasporitic	4	25	100	44	16,55	48,05	4,17	8,32
Alite, leptochloritic	5	6	280	93	24,70	40,65	3,16	8,94

tinguishable from them, in which the Al₂O₃/SiO₂ ratio varies with the limestones from 1.8-2.0. The alites, in turn, may turn into corundum-mica rocks, in which chlorites and micas predominate and a certain amount of corundum is present, and finally into micaceous shales.

Analysis of the data we obtained on the boron content in bauxites and enclosing rocks of the Obukhov deposit (Table 3) reveals three very characteristic features in the overall picture of its distribution in this deposit. First of all, there is the extremely low boron content in the dikes of different rocks which cut across the deposit; secondly, there is the higher boron content in alites in comparison with bauxites and thirdly, there are the exceptionally wide limits of variation in boron content in all the formations which make up the ore body. The last feature also graphically confirms the nature of boron distribution in the bauxites and alites in the separate sections (Table 4). One must keep in mind that hole 815 which we studied (central-lateral area) went approximately along the dip of the ore body and several times cut across bauxites and alites at different depths, and thus, as is seen, a severe nonuniformity in boron distribution is peculiar even to ores which were originally formed at the same "stratigraphic" level. The same nonuniformity in boron distribution is also observed in bauxites of the overlying intra-Eifelian ore horizon of the Obukhov deposit, where boron content varies from 22 to 700 g/ton (hole 054, same area).

On the whole, of the bauxites studied from the Obukhov deposit, four types of section may be distinguished, which differ in character of distribution and level of boron content: 1) sections with very low boron content: 17-30 g/ton (holes 238 and 107); 2) sections with the usual content: 40-70 g/ton (holes 301 and 65); 3) sections with boron distribution highly variable with depth, variations from a few dozen g/ton to 1400 g/ton (holes 815 and 054); and 4) sections with a consistently high content of the study element: 950-1200 g/ton (hole 483).

It must be mentioned that this feature of the Obukhov deposit is also very evident from comparisons with the variation limits for boron content in ores of the deposit considered and of other deposits (see Table 1), and especially in the Berdsk-Maya deposit (see Table 3), which was not affected, as was noted above, by the metamorphic action of intrusive rocks.

As it seems to us, all the material presented above indicates, with a high degree of probability, the association of anomalous boron content in ores of the Obukhov deposit both with their metamorphic transformation under the influence of intruded adamellites and with metasomatic introduction of boron into the bauxites and alites. In any case, no other hypotheses occurred to the authors to explain the high boron content in the bauxites of this deposit.

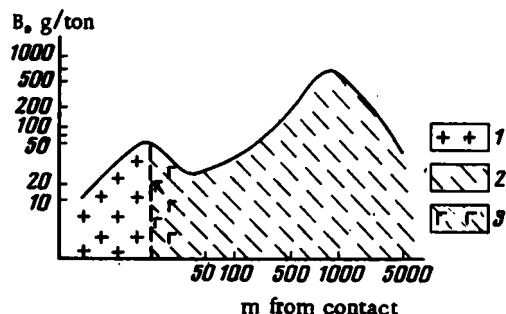


Fig. 2. Change in boron content in the contact zone of granites and metamorphic slates (Harz mountains, East Germany, Harder, 1967). 1) Granites; 2) slates; 3) contact hornfels.

TABLE 4. Change in Boron Content in Bauxites and Alites of the Obukhov Deposit (central-lateral area, hole 815)

Sample No.	Interval, m	B, g/ton	Wt. %			
			Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	FeO
57	183,85—185,1	28	12,00	58,70	2,30	13,68
59	185,52—187,30	130	13,80	57,30	3,70	12,46
63	194,60—195,07	32	14,00	56,00	3,50	11,34
69	229,51—230,87	1400	27,60	40,20	0,86	12,33
101	232,10—236,76	1200	28,20	40,20	1,92	8,96

It must be noted, in general, that the elevated boron content of the exocontact zones of intrusives, including those of acidic composition, is a very widespread and well-known phenomenon (Aleksandrov et al., 1968; Lisitsyn, 1974).

Interesting and to a certain degree similar to the case considered is the sharp increase in boron content in the exocontact zone of a granite intrusion breaking into metamorphic slates, which is described in the Harz mountains (East Germany) by H. Harder (1967) (Fig. 2). As is seen, the slate portions are enriched in boron by more than 10 times. We turn our attention to the fact that at more than 1000 m from the contact, boron content in the slates suddenly begins to decrease and again suddenly reaches the values usual for these slates. V. L. Barsukov (Aleksandrov et al., 1968) presented an example of the penetration into sandy shale rocks, near their contact with a granite dike containing an elevated amount of tourmaline, of veinlets from the neoformations of this material. It is thought not necessary to continue the series of similar or approximate examples, since, as we have already noted above, this phenomenon is quite ordinary.

One must also pay attention to the fact that boron is a constant and very characteristic element in many, many types of gaseous precipitates, condensates, hydrothermal waters, and their associated sediments in practically all areas of modern active volcanism. Thus, the content of H₃BO₃ in the fumarole gases of New Zealand reaches 730 mg in 1 liter of steam (Ellis and Sewell, 1963). High-temperature volcanic waters contain boron in amounts from 4 to 36 g/ton (Mizutani, 1962). Concentrations of boron in highly mineralized water, pumped from a depth of about 1500 m in southern California (Salton Sea), are 500 g/ton, while in the precipitate which settled from this water, they are 0.15% (White et al., 1965).

Let us turn now to the Vezhayu-Vorykvino deposit of bauxites in central Timan, for whose ores an anomalously high boron concentration is characteristic. The deposit is located within the southeastern part of the Chetlass ridge.

Bauxites in the bauxite-bearing laterite cover of zonal structure lie upon carbonate-shale and shale-carbonate rocks of the Bystrin suite in the Riphean basement. They are covered by sedimentary and volcanic-sedimentary rocks of the Pashiya-Kynov horizon in the Upper Devonian. In the bauxite-bearing bed, three members are distinguished: the subore, ore, and superore (Abramov et al., 1975).

The subore member is represented by argillaceous weathering-crust formations which are ferruginous to varying degrees (sialites, alites), which developed along carbonate-shale

TABLE 5. Boron Content in Bauxites and Enclosing Rocks of the Vezhayu-Vorykvino Deposit (central Timan)

Rock	No. of samples	Av. content, g/ton	Wt. %			
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO
Clays, superore, hydromicaceous-kaolinite	30	175	37,0	29,7	12,8	2,6
Alites, superore	36	181	24,4	40,0	12,8	5,0
Bauxites	57	125	9,3	49,6	19,3	4,1
Alites, subore	19	117	21,2	37,4	17,2	8,0
Clays, subore, hydromicaceous and kaolinite-hydromicaceous	18	126	40,4	29,4	14,8	0,2
Shales of the Bystrin suite, Riphean (orig. rocks)	2	89,0	61,4	17,2	3,5	3,4
Dolomites of the Bystrin suite, Riphean	6	40	12,0	6,6	0,62	1,40
Basalts	7	6	50,1	13,9	4,9	8,2
Basalts, metasomatically altered	5	116	43,9	18,8	16,7	1,1
Basalts, altered by new supergene processes	3	34	43,1	18,7	16,7	23,8
Tuffs	4	36	45,9	14,8	7,8	7,8
Tuffs, weathered out	7	65	42,8	21,4	12,6	3,3

rocks of the basement. Preservation of the structural and textural indices of the original Riphean root-zone rocks is characteristic of the rocks in this bed. Based on mineral composition, the clays are here subdivided into sericite-hematitic, kaolinite-hematitic, and kaolinite-sericitic composition. Among the accessory minerals tourmaline, zircon, rutile, hornblende, pyrite, zoisite, etc. are distinguished. In the upper part of this member, chamosite appears. The thickness of the member is from several meters to 50-70 m. The transition boundaries of the subore ore member into the ore lying above are usually gradual from sialite through alite to bauxite.

The bauxites lie primarily on subore clays and only occasionally on the carbonate rocks of the Bystrin suite. Their thickness varies from 0.5 to 30 m, being 9-10 m on the average. In individual sections, the bauxites are interbedded with argillaceous rocks (the thickness of the laminae is from 0.1 to 3-5 m), analogous to the subore-member formations mentioned above. The fundamental rock-forming minerals of the bauxites are boehmite and hematite, and chamosite and kaolinite to a lesser degree. Also noted are diaspore, goethite, hydromica, chlorite, corundum, dickite, epidote, and zoisite. Of the accompanying minerals, zircon and tourmaline are most widespread.

The superore member is composed of rocks which to one degree or another are enriched in alumina (alites, sialites). However, the mineral predominant in it is kaolinite. The overlying deposits of the Lower Frasnian substage of the Upper Devonian are represented by terrigenous (siltstones, shales with pyrite), volcanic-sedimentary, and effusive rocks (basalts, tuffs, tuffites). Their maximum thickness is about 200 m.

Essentially important for the further analysis of boron distribution patterns in the bauxites considered is the fact that the bauxites of the Vezhayu-Vorykvino deposit, like the bauxites of the Obukhov deposit, are characterized by distinctly manifested traces of superposed processes, most probably associated with temperature and hydrothermal effects of the intrusion of gabbro, which is revealed at some depth, from geophysical data (Plyakin, 1973; Dubov, 1975), and the intrusion of basic dikes which cut the ore bodies.

The covering basalts also were subject to noticeable changes, primarily along zones of tectonic dislocation. A study of the nature of mineral and geochemical changes in the basalts has permitted the establishment of the wide development of potassium metasomatism (Mamedov et al., 1976).

With hydrothermal activity the chamotization of the bauxites in the majority of cases studied is associated. Near the contact with the dikes, the ores are occasionally almost completely turned into chamosite complexes. In other like areas and in the zones of tectonic dislocation, dark gray and black magnetite bauxites are noted, in which there are diaspore, corundum, and magnetite. Occasionally formations of the corundite type also occur here with a very high Al₂O₃ content (up to 70%) (Dubov, 1975). Metasomatic ores, represented

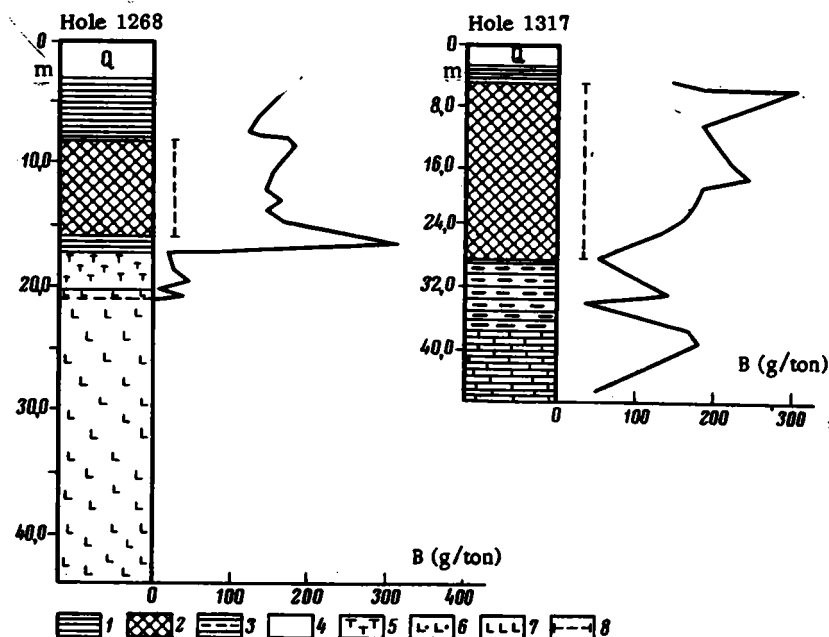


Fig. 3. Change in boron content in bauxites and enclosing rocks of the Vezhayu-Vorykvino deposit: 1) Alites; 2) bauxites; 3) hematite-chamosite rock; 4) dolomitized limestone; 5) tuffs; 6) altered basalts; 7) basalts; 8) average content (clark) of boron in bauxites.

by dense varicolored (mainly black and greenish-gray), sometime jasperlike hornfelsic varieties which are chamositized, are confined to the near-contact zones of the bauxites and the basalts covering them (Abramov et al., 1975).

We studied boron content in all the basic varieties of bauxites and their enclosing rocks in the Vezhayu-Vorykvino deposit in central Timan (Table 5). Analysis of the data presented above all permits one to state that boron "contaminates" the rocks of practically all the section studied, from carbonate and shale rocks of the Riphean and the argillaceous and bauxitic rocks overlying them to the overlying bauxite-bearing member of subore, hydromica-kaolinite clays. The effusive rocks are also characterized by a clearly elevated boron content. The fact draws attention that the more argillaceous rocks both in the Riphean and in the overlying formations have a higher boron content. This may be considered entirely understandable, if one considers that the basic mechanism of boron bonding is its sorption.

The more detailed features of changes in boron content in two actual and sharply differing sections of the ore body in the Vezhayu-Vorykvino deposit are easily seen in Fig. 3 (holes 1317 and 1268). From a consideration of the graphs, it becomes clear that boron is quite nonuniformly distributed in the bauxite horizon and the basalts which were not effected by any alterations; they are characterized by extremely low boron contents (6 g/ton) and only their weathered parts, as well as the tuffs, display a somewhat higher amount of this element. Structural clays which developed along the tuffs (hole 950) contain from 80 to 150 g/ton of boron.

It is especially necessary to note that changes in boron content in the bauxites not affected or hardly affected by superposed supergene processes (such as the section through which hole 2231 passes) are much more severe, while the concentration of this element in similar bauxites is perfectly "normal" and comparable to boron content in the ores of other platform deposits (about 50 g/ton).

It seems to us that in the ores of the Obukhov and Vezhayu-Vorykvino deposit, the elevated boron content is associated with the effect of intrusive and volcanic processes and hydrothermal-metasomatic phenomena.

Thus, up until the present time two reasons were presented for the appearance of anomalously high boron content in bauxites: 1) the occurrence of boron in the rocks original for the bauxites, mainly in accessory tourmaline (or terrigenous tourmaline, for sedi-

mentary rocks), which was relatively well-preserved in the process of laterite weathering and which accumulated, hindering the removal of boron, and 2) the superposition on the bauxites of hydrothermal-metasomatic processes associated with intrusives or volcanic phenomena close to these deposits. In the last case, boron, as the most characteristic element of gas-liquid fractions, is sorbed by surface-active minerals and, as is seen, is even accumulated to a definite degree in weathering products and sediments.

The ascertaining of these new features in the precipitation and accumulation of boron in bauxites must be studied further not only with the aim of learning the genetic history of the deposits but possibly also for purposes of application, in evaluating the degree of action upon bauxites of hypogene processes affecting their quality.

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Of the placers in the central cis-Dnepr region, the deposits of the near-shore-marine type have fundamental industrial significance, having a complex composition of useful components which formed mainly due to the nonuniform reworking and redeposition of products of the late Mesozoic crusts of Precambrian-formation weathering. The original sources of these placers are various crystalline rocks, having one type of ore mineralization or another, which is occasionally poor. Of the ore sources, there are no analogues for the placers relative to the scale of mineral-resource composition. The available factual data do not confirm the hypothesis of certain investigators of the presence, among ore-bearing sands, of "active" and "passive" fractions, which is supposedly evidence of the formation of placers due to the erosion of individual, large original deposits and the accumulation of grains of the "passive" fraction.

The central cis-Dnepr region is one of the large regions of placer-deposit distribution of various genetic types: eluvial, deluvial, alluvial, near-shore-marine, and shallow-water sea. The near-shore-marine placers have the greatest practical significance, being distinguished by a high level of concentration and large reserves of useful components. These placers are limited to the bed of Poltavian-Sarmatian quartz sandstone and are traced in an interrupted band in a northwesterly direction in the join zone of the Ukrainian shield and the Dnepr-Donets basin (Fig. 1). The deposits of the central cis-Dnepr region make up the eastern limb of the cis-Dnepr placer zone, which is traced from Volynia to the cis-Azov region.

The placer deposits of the central cis-Dnepr region contain ilmenite (leucosene), rutile, zircon, sillimanite, kyanite, staurolite, and more rarely monazite, garnets, and other minerals, i.e., they belong to the polymineralic complex type of placer. As I. I. Malyshev and other investigators indicate, placers of these minerals ("light" metals), in contradistinction to placers of gold and platinum, pass through several stages of formation, during which the stage of thick crust-formation is obligatory, in the process of which the parent rocks undergo intense disintegration and chemical decomposition with the release and concentration of stable minerals, due to the removal of alkalies, magnesium, calcium, and other highly mobile elements.

Various opinions are voiced on the question of the original sources of the nearshore-marine placers in the central cis-Dnepr region. The majority of authors consider that these sources are associated with various crystalline shield-rocks, most often on a regional scale, and that placers may also be formed and most often are formed due to the destruction and repeated reformation of the products of destruction from nonrich and even poor ones. There are no complete analogues to the cis-Dnepr placers among the original deposits of ore occurrences of the region. Other investigators admit the possibility of there existing ore-bearing zones which are contrasted with the placers, which are the fundamental suppliers of accessory minerals.

N. T. Vadimov (1958) allows that the fundamental source of titanium minerals in the central Dnepr placers are gabbroic rocks of the Korsun'-Novomirgorod pluton. However, paleogeographic data and the significant distance of the placers from the pluton contradict this. In the opinion of A. V. Khrîpkov (1971), the placers of the central cis-Dnepr region are directly projected onto zones of fault disruption with an elevated titanium content in the original rocks. The input for such a condition is the author's ideas of the presence of "active" and "passive" fractions of ore minerals, based on analogy with the gold-bearing

Dnepr Group of the IMR Divisions, Dnepropetrovsk. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 60-67, November-December, 1977. Original article submitted February 23, 1977.

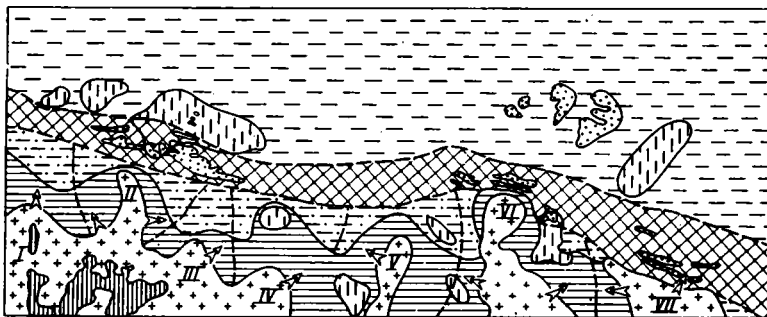


Fig. 1. Sketch of the paleogeography of the Paltavian era and distribution of nearshore-marine placers in the northern part of the central cis-Dnepr region. 1) Crystalline rocks of the basement with weathering crust (uplifted portions of the buried relief); 2) sedimentary deposits of pre-Paltavian age; 3) area of slope of the basement outcrop for a submerged sea at its highest level; 4) area of repeated interchange of continental and nearshore-marine conditions; 5) lagoon, temporary; 6) shallow-water sea; 7) stable beach zone; 8) placer contours; 9) ancient river; 10) direction of fundamental removal of terrigenous material. Outcrops of the basement (based on elements of buried relief): I) Ingulets; II) Pyatikhat; III) Sofiya; IV) Bazavluk; V) Dnepr; VI) Sinel'nikov; VII) Volch'ei.

placers in the northwest of the USSR. With the slight gradient of ancient plains rivers, they carried out only the "active" fractions of the stable minerals, while the "passive" fractions accumulated near the original sources. Consequently, where the placers are, there must be their original sources. These and similar conclusions are for the most part theoretical and do not agree with the factual data. An answer to the question of the original sources of placer deposits is possible on the basis of factual data on ore and placer deposits, their structure, formation conditions, distribution, etc.

The ore sources of placer deposits on the Ukrainian shield are the metal-bearing crystalline rocks of its Precambrian basement. The investigations of Ya. N. Belevtsev, M. I. Ivantishin, I. L. Lichak, N. P. Semeenko, I. S. Usenko, I. D. Tsarovskii, and others have established the metallogenic specialization of various complexes and types of crystalline rocks. These minerals have been most fully generalized and presented in the monograph "Metallogenesis of the Ukraine and Moldavia" in 1974. It is established that the fundamental bearers of the most widespread minerals in titanium placers are rocks of a basic character — gabbro, gabbro-norite, gabbro-anorthosite, etc. With these rocks are associated original deposits of ilmenite and apatite of the Irtys-Trostanets interfluve (Korosten pluton) and the right-bank region of the Dnepr (Korsun'-Novomirgorod pluton), where alluvial and deluvial-alluvial placers are located near massifs and the ore-bearing weathering crust. In other regions, the suppliers of titanium minerals are also diabbases, amphibolites, schists, and gneisses, and granitoids to a lesser degree. Zircon is associated mainly with alkalic rocks (the nepheline syenites of the Oktyabr' massif in the cis-Azov region, etc.), more rarely with granites and migmatites; however, large accumulations of zircon are unknown in acidic rocks. The basic sources of monazite are granites and migmatites of the Chudno-Berdichev type, as well as rosy aplite-pegmatoid varieties of granites. Apatite and tantaloniobates are characteristic of carbonates, and cassiterite of young alkali granites. The sources of sillimanite, kyanite, and sauroilite are the most ancient gneisses and schists in the shield.

Numerous Precambrian rocks which are fundamental bearers of ilmenite, rutile, zircon, and monazite are uncharacteristic of the central cis-Dnepr region, although it is rich in complex placers. The weighted mean content of titanium in the Precambrian rocks of the central cis-Dnepr region as a whole is lower than the clark and is 0.39% in all, varying from

TABLE 1. Content of Basic Placer Minerals in Crystalline Rocks of the Volch'ei Outcrop (generalized data of A. A. Nastenkov, 1958; El'yanov et al., 1964)

Rocks	Content, kg/m ³													
	ilmenite		rutile		zircon		monazite		sillimanite		kyanite		sphene	
	av.	max.	av.	max.	av.	max.	av.	max.	av.	max.	av.	max.	av.	max.
Granites	0,54	2,30	0,025	0,91	0,46	2,07	0,02	7,80	0,84	3,75	Sig.*	—	—	2,97
Migmatites	0,58	50,0	0,02	0,85	0,35	5,98	0,11	2,40	3,42	29,2	—	—	—	98
Gneisses	0,54	10,2	0,03	0,30	0,13	1,24	0,03	0,44	2,36	2,70	—	—	—	26
Amphibolites	2,21	11,0	Sig.*	—	0,81	1,50	Sig.*	—	2,58	5,90	—	0,20	—	8
Pegmatites	—	—	—	—	0,25	—	1,06	1,22	0,50	1,01	Sig.*	—	—	2
Granodiorites	Sig.*	121,0	—	—	0,69	1,82	—	—	1,40	2,33	—	—	—	5
Weathering crust from acidic rocks	1,21	19,8	0,07	1,42	0,67	14,5	0,06	1,0	0,85	1,43	—	—	—	70

*Significant.

TABLE 2. Content of Basic Stable Minerals (concentrate) in the Weathering Crust of Crystalline Rocks in the Verkhovtsev Region (based on the data of I. F. Zlobenko, 1957)

Parent rock	Concentrate	Content, kg/ton								
		ilmenite	leucocoxene	rutile	zircon	kyanite + sillimanite	staurolite	tourmaline	garnet	others
Biotite - plagioclase gneiss	3,20	0,26	0,23	0,03	0,06	Tr.*	0,02	Tr.*	0,74	2,56
Amphibolite	32,50	3,67	1,10	0,15	0,03	0,14	0,01	—	—	27,40
Talc - chlorite schist	6,59	0,03	0,08	3,59	0,03	0,73	0,12	0,01	—	2,0
Chlorite schist	6,18	0,02	0,04	0,72	Tr.*	—	Tr.*	Tr.*	—	5,40
Quartz - sericite schist	1,50	0,01	Tr.*	0,40	0,05	0,01	—	—	—	0,03
Migmatite of plagiogranite	25,22	1,90	0,13	Tr.*	0,03	Tr.*	—	—	—	23,16
Kirovograd granite	3,50	0,35	0,09	0,06	0,05	0,10	0,60	Tr.*	0,47	1,72
Charnockite	0,22	0,03	0,07	0,01	0,05	Tr.*	Tr.*	—	Tr.*	0,04
Polymigmatite	2,50	0,34	0,06	0,02	0,03	0,07	0,01	—	—	1,98
Migmatite of gray granite	10,63	Tr.*	0,01	0,01	0,12	—	Tr.*	—	—	10,53
Aplite - pegmatite and granite and its migmatite	18,19	3,76	5,23	0,20	0,07	0,02	0,03	0,05	0,01	8,82

*Traces.

0.12% in the Dnepr granites to 0.9-1.68% in the amphibolites and other rocks. The average content of ilmenite, rutile, and zircon in granitoids, based on the data from 164 analyses, is 445, 22, and 344 g/m³, respectively (ratio 1.29:0.64:1) (El'yanov et al., 1964). In Table 1, data are presented on the content of ilmenite and other minerals in crystalline rocks of the Volch'ei outcrop.

With the total low ilmenite and rutile content in the central cis-Dnepr territory, individual portions are exposed with a high concentration of these minerals. Based on the data of A. I. Andreev, B. A. Solos'ei, and others (1971, 1973), a high ilmenite content is established in diabase dikes of the Kamen region of the Volch'ei outcrop. The dikes are confined to fractures with a northwesterly trend. Mineralogical composition: plagioclases 40-50%, pyroxenes up to 40%, magnetite 5-10%, ilmenite 5-10%. An ancient weathering crust is well developed on the diabases, the thickness of which is from 15-20 to 60-70 m. Ilmenite content in the weathering crust is several dozen kg/m³. Zlobenko (1957) described the development in the region of Savro station of a band of rutile-bearing schists 150-200 m wide, containing rutile up to 11 kg/ton (average 1.5-3.0 kg/ton); amphibolites near the village of Krasnyi Orlik contain 1.5-3.0% TiO₂. V. I. Sereda et al. (1963) described a high content (up to 20-30%) of sillimanite in gneisses of the Volch'ei outcrop and an elevated content of monazite in granites in the Vasil'kovka village region (lower reaches of the Volch'ei River).

In all the Precambrian crystalline rocks of the central cis-Dnepr region, a post-Mesozoic weathering crust is widely developed and relatively well preserved, reaching a thickness of 100-120 m over the full vertical profile. In the crust, a complex of ore and accessory minerals is established, whose content in comparison with the parent rocks is increased about double. In Table 2 are presented the contents of ore minerals in the weathering crust of the most widespread crystalline rocks of the Verkhovtsev region. The ratio of ilmenite, rutile, and zircon in the eluvial bed is 2.05:0.13:1, respectively. Compared to the parent rocks, the role of titanium minerals in the crust increases, which possibly occurs due to the destruction of sphene and the crystallization of titanium dioxide in the decomposition of biotite and other minerals.

Against a general background of a relatively poor ore-bearing weathering crust, individual rich areas are distinguished. Besides the above-mentioned Kamen region, we note the weathering crust of gneisses near Nezabudino station, which contains up to 146.34 kg/m³ of ilmenite (I. F. Zlobenko, 1957), the eluvia of granites in the Sursk region with a zircon sampling of 109 kg/m³, and others. Such "hurricane" contents are not unique, but they are characteristic only of disconnected portions which are small in area. In addition, considering the large area of weathering-crust distribution, its significant thickness of several dozen meters, and its universal saturation to one degree or another in ore and accessory minerals, it is easy to determine that the total reserves of stable minerals released during supergene processes were huge, and this was a very favorable basis for the formation of large, rich placers. As for the areas with a high content of ore components in diabases and other rocks (the Kamen dikes and others), it is impossible to consider them as the direct sources of mineral placers. Based on the volume of rocks subjected to weathering and erosional downcutting (the total amount of the ore mass), they are significantly inferior to the placers. Besides, it is evident that the preservation on the dikes of a thick weathering crust bears witness against the possible hypothesis that they were the fundamental sources of the Volch'ei placers.

The placers were formed due to the transformation and repeated reworking of the products of destruction of various crystalline rocks over large areas; this assured their complex composition, significant reserves, and high concentration of ore components.

The content of ore minerals in the nearshore-marine placers of the cis-Dnepr region increases, in comparison with the crystalline rocks and weathering crust, 10 or even 100 times. Although the amount of ore minerals varies within broad limits, their ratio in each placer remains more or less constant. According to the data of I. I. Malyshev (1957), the heavy concentrate of the cis-Dnepr placers contains 13-17% rutile, 32-37% ilmenite, 9-11% zircon, and about 40% of nonore minerals (kyanite, staurolite, sillimanite). According to our data (El'yanov et al., 1964), the ratios of the average content of ilmenite, rutile, and zircon vary in the following way: in placers from the right bank of the Dnepr, it is equal to 6.5:1.8:1, respectively, in left-bank placers 6:1.5:1, and in placers of the Dnepr-Donets basin 2.7:1.5:1. These data confirm the strong differentiation of terrigenous material. The farther the placers are from the source of removal (the Ukrainian shield), the more the role of zircon increases and the more the relative significance of ilmenite decreases, although it remains the dominant mineral in all the placers. This must be explained by the higher stability of zircon.

Supporting the ideas presented on the significant detachment of the placers from the primary origin, there are also data on the grain-size composition of quartzose sands and ore minerals, the finely bedded structure of the placers, and the conditions of their deposition. The grain-size composition of the sands is distinguished by a high constancy and uniformity. From 70 to 100% of the mass consists of grains 0.5-0.05 mm in size, while the basic fractions are 0.25-0.1 and 0.1-0.05 mm. Particles less than 0.05 mm make up only 10-15% of the sand mass, but are constantly encountered. Small variations in the median size of the grains (average 0.11 m) and the sorting coefficient, equal to 1.59, confirm the high level of uniformity in the enclosing rocks. Toward the Dnepr-Donets basin, a constant, although not very great, size reduction in the sand is observed, the median grain size of which is 0.14 mm on the shield slope and 0.10 mm in the basin. There exists a definite interrelationship between the grain-size composition of the enclosing rocks and the ore minerals. As a rule, quartz grains are larger than the grains of ore minerals. The size of the quartz is 0.15-0.2 mm, and in the ore concentrate, particles 0.05-0.15 mm in size predominate.

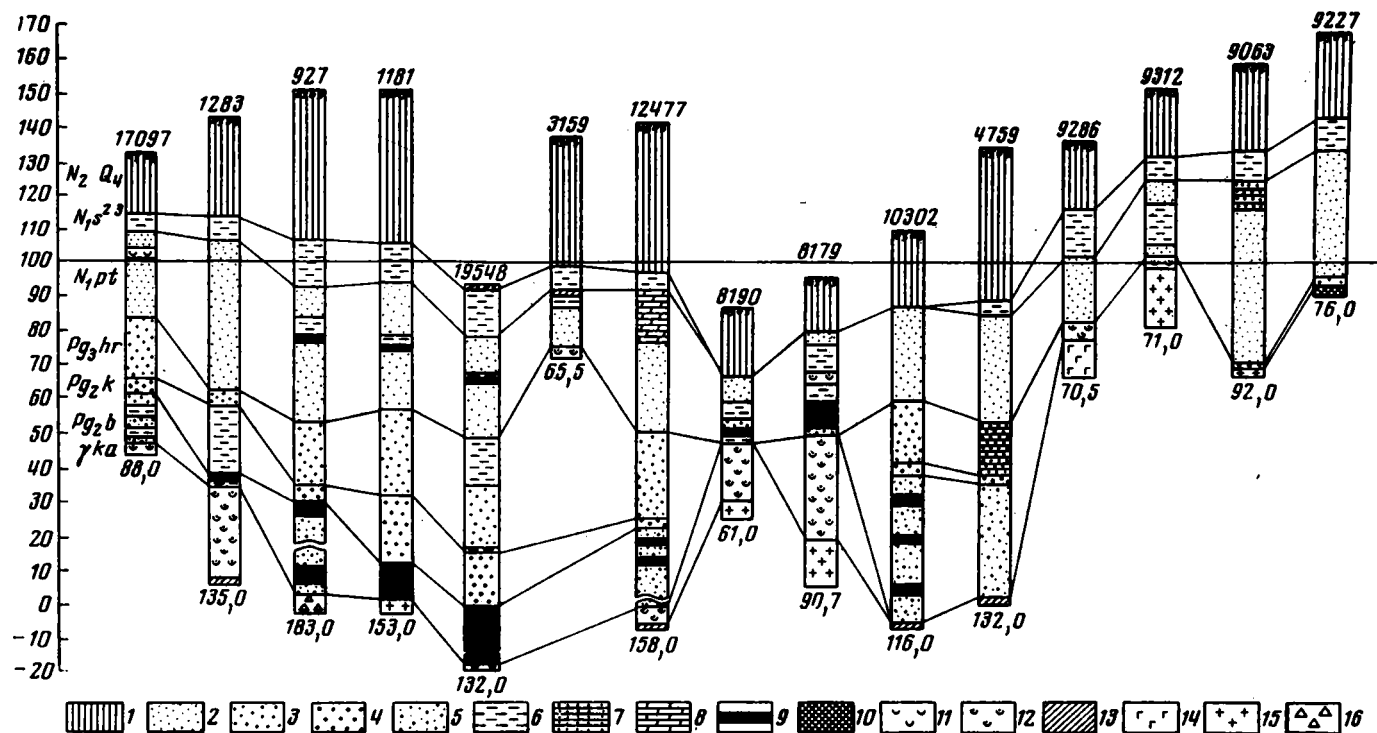


Fig. 2. Type sections of Cenozoic deposits in the central cis-Dnepr region. 1) Loams and red-brown clays; Neogene-Quaternary; 2) white quartz sands, Poltavian-Sarmatian; 3) quartz-glaucinite sands, Kharkovian; 4) sands, quartzose, tripolilike, limy, glauconitic, Kievian; 5) sands of various grain-sizes, Buchakian; 6) variegated clays, Sarmatian; 7) sand-clay rocks, Buchakian; 8) limestones, Sarmatian; 9) brown coals, Buchakian; 10) limestones, Carboniferous; 11) secondary kaolins; 12) weathering crust of crystalline rocks; 13) crystalline schists; 14) basic rocks; 15) granitoids; 16) gravel of crystalline rocks.

N. T. Vadimov made some inquiring calculations, on the basis of which the ratio of the size of quartz grains and ore minerals from the right bank of the Dnepr (1:0.61) is approximately identical to the inverse ratio of the specific gravity ($4.0:2.7 = 1:0.68$). We note also that the quartz grains and ore minerals are distinguished by a high level of rounding; such grains comprise up to 80-90% of the central mass along the strike of part of the placers.

The data presented refute the possibility of dividing the ore minerals into "active" and "passive" fractions, since they are all reduced in size to extreme limits (Zenkovich, 1958) and have repeatedly undergone significant displacement. Consequently, the whole mass of sands and other minerals is introduced from outside and was not formed "in place," as it seemed to A. V. Khripkov.

The productive bed of quartzose sands in the central cis-Dnepr region, of Poltavian-Sarmatian age, is the upper part of the Cenozoic deposits, characteristic sections of which are presented in Fig. 2. In the complete section of the sedimentary bed, whose thickness is from 70-90 to 130-150 m, the sands are underlain by deposits of the Kharkov, Kiev, and Buchak suites and by a weathering crust (the thickness of the latter is usually 20-30 m, and sometimes up to 70-100). In the abbreviated section of the sedimentary deposits, formations of the Lower Paleogene come out, and the soil of the Poltavian-Sarmatian sands is that of deposits of the Kharkov suite or the immediate weathering crust. In areas with similar sections, the thickness of the sedimentary deposits is 35-50 m in all. The thickness of the productive sands is usually 35-40 m, and is up to 60-65 m in places.

The complete stratigraphic section of Cenozoic deposits is characteristic of the placers on the right bank of the Dnepr, and the incomplete section for the placers in the region of the Volch'ei outcrop (left-bank part of the Dnepr). This outcrop occupies, in the central cis-Dnepr region, a dominant hypsometric position with absolute surface indications of the Precambrian rocks and weathering crust up to 180 m. Corresponding to this, the productive sands here lie 20-40 m higher than the placers in the right-bank section. A high level of development and preservation of the ancient crust is characteristic of the Volch'ei outcrop, the crust reaching a thickness of 100 m, with which is associated very large deposits of kaolins (the Prosyanyov group). They contain a certain amount of monazite and other accessory minerals and from these positions, they can be considered to be eluvial placers, small in scale due to the low concentration of ore minerals.

Data on the solid discharge of modern rivers (Strakhov, 1962) indicates that they carry off every day a huge amount of clastic material, being not inferior in this respect to the rivers of mountainous lands. On the whole, over the Ukrainian shield, it is calculated (Litvinenko and El'yanov, 1967) that in more than 60% of its area, the thickness of the weathering crust does not exceed 10 m, while its original thickness is estimated at 100-120 m. This confirms the intensity of erosional-denudational processes. Also speaking in support of this is the large number of sedimentary deposits which are formed due to the transport and redeposition of the late Mesozoic crust. We have in mind the deposits of secondary kaolins (Polozhsk, Novoselitsk, and others), bauxites (Smelyansk), and others.

Poltavian rivers carried off into the sea a huge amount of clastic material which was subjected to the action of shoreline processes in the near-shore zone, a major factor in which is wave processes. In near-estuary areas of the rivers, maximum concentrations of sands and ore minerals are observed. Terrigenous material was dispersed by near-shore currents along the shoreline of the Poltavian sea, forming placers which extended in a north-westerly direction.

The studies of V. P. Zenkovich (1958) and other authors have shown that one of the leading processes of hydrodynamics going on in the shore zone is that of wave movements. They accumulate debris along the shore, expanding the shore zone, or else they destroy the shore or maintain its stable contour. Wave processes lead to the occurrence, along shore currents, of debris whose width reaches 1-2 km, and length tens or hundreds of kilometers. The transverse and longitudinal displacement of the debris leads to the formation of large accumulations of sand, the grain-size differentiation of clastic material, and its enrichment in heavy and stable minerals, i.e., a natural concentration occurs with a stratification characteristic of it.

In an analogous way, the placers of the central cis-Dnepr region were formed in the near-shore zone of Poltavian and Sarmatian seas. The rectilinear contours of the deposits confirm the slightly carved-out shoreline in the areas between the estuaries of the entering

rivers. Depending on the back-and-forth and tidal oscillations in sea level, the seasons, and other reasons, the shoreline was partially displaced, which contributed to a continuous washing out and concentration of the sands, i.e., the formation of placer deposits. The formation of placers went on with a developed stable profile of equilibrium (in the meaning of V. P. Zenkovich) and the slow submergence of the shoreline.

Various notions on the original sources of the nearshore-marine placers of the cis-Dnepr region orient the directions of survey work differently. If we depart from the bonds of placers to definite original deposits, this survey front is sharply constrained. On the other hand, departing from notions of placer formation due to regional and frequently poor ore sources, the front of survey work and discovery prospects for new deposits increases. Of the survey indications, first place falls to favorable paleogeographic conditions, which must be studied in detail. Besides searching for new complex placers (ilmenite, rutile, zircon, etc.), it is necessary to do careful testing for gold, diamonds, scheelite, and other valuable components.

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AUTHIGENOUS CLAY MINERALS IN LATE PRECAMBRIAN DEPOSITS OF THE ENISEI

RANGE

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UDC 552.14:551.72(571.51)

Study of the distribution of clay minerals in the Late Precambrian section across the Enisei Range shows that mainly allothigenous minerals of the dioctahedral type are accumulated at the initial stage of two transgressive-regressive cycles, under conditions of cation deficiency. In contrast to that, the terminal stage of these cycles (basin isolation) is marked by intensive authigenous mineralization at an excess of cations. The character of the newly developing phases depends on thermobaric conditions of the medium.

Introduction

Reading upward, Late Precambrian deposits of the Enisei Range are subdivided into the Lopatino, Vandady, Chivida, Sukhtalma, and Nemchany suites or their analogs. Their total thickness is about 6000 m, indicative of an intensive compensated-for subsidence of the region (Khain et al., 1967). Deep subsidence of the accumulated sediments resulted in their very significant post-sedimentation alteration: primarily a high general aggradation of

Moscow State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 68-84, November-December, 1977. Original article submitted November 20, 1974.

three-layer clay minerals and also their different character in argillaceous and silty arenaceous rocks.

The most complete study of clay minerals in Late Precambrian deposits of the Enisei Range was done within the Teya-Chap and partly Vorogov synclinoria. The lower part of the section is represented by the Lopatino suite, some 500 m thick, of red quartz sandstones, siltstones, and argillites, with a 2.5-3.0-m-thick bed of coarse clastic conglomerates at the base. A horizon of light-gray dolomites, not over 80 m thick, completes the section. The overlying Vandady suite, largely gray, about 900 m thick, is made up in the lower and middle parts by quartz sandstones, with argillites containing stringers of siltstones, sandstones, gravelstones, and carbonate rocks in the upper part. Their overlying Chivida suite, about 700 m thick, largely green-gray, is represented by flysch-type rocks: polymictic sandstones and "tillites" with stringers of tuffs and tuffaceous sandstones. The next higher Suktalma suite, 600-1000 m thick, is different in different areas of the Enisei Range. Along the Teya River, to the northeast, it consists largely of red arkosic sandstones and siltstones and also dolomites. In the northwestern part, along the Stolbovaya and Isakovka rivers, it is represented mainly by dolomites with thin (15-20 cm) stringers of green-gray polymictic sandstones and siltstones of graywacke composition.

The Late Precambrian section is capped by over 2500 m of the coarse-clastic, largely red Nemchany suite. Its lower part, 350-400 m thick, is represented by siltstones and argillites with occasional stringers of arkosic, less commonly quartz and polymictic sandstones. The role of siltstones and argillites is reduced in the middle part; the upper part of the suite is predominantly coarse-grained sandstones, gravelstones, and small-pebble conglomerates.

In addition, clay minerals were studied in the Moshakovsk suite identified only in the northwestern part of the Kansk-Taseevsk through where it is represented by red siltstones and also arkosic and polymictic sandstones. Stratigraphically, this suite occurs between analogs of the Chivida and Suktalma suites of the Enisei Range.

Clay Minerals in Argillites and Highly Argillaceous Siltstones

According to diffractometric studies, clay minerals in Late Precambrian argillites and highly argillaceous siltstones (Figs. 1 and 2) are represented mainly by dioctahedral hydromica with a subordinate and variable addition of ferromagnesian chlorite (Kotel'nikov and Solodkova, 1971, Solodkova and Kotel'nikov, 1971). According to electronographic studies, hydromica is characterized by the following parameters of the elementary cell: $a = 5.17-5.21$; $b = 8.96-9.02$; $c = 19.8-20.1 \text{ \AA}$; $\beta = 95^{\circ}30'-96^{\circ}$ and belongs to polytype modification $2M_1$. In addition to the pseudoisometric-tabular habit of the particles and polymictic modification $2M_1$, the allothigenous character of hydromica in argillaceous rocks (Vikulova, 1952; Kotel'nikov, 1963, 1965; Weaver, 1956) is in turn indicated also by a different degree of mineral aggradation in the several horizons, regardless of their position in the section. This suggests that the $2M_1$ modification, known to be not only allothigenous but also originating in profound alteration of rocks at the metagenesis stage, reflects in our instance the character of source material from the denudation areas.

From diffractometric studies, chlorite in argillites and highly argillaceous siltstones of the several sequences is characterized by different relationship of reflexes. Correspondingly, parameters of the elementary cell of the mineral vary within the following ranges: $a = 5.30-5.36$; $b = 9.17-9.28$; $c = 14.5 \text{ \AA}$, and $\beta = 97^{\circ}-97^{\circ}10'$. This indicates certain fluctuations in the chemical composition of chlorite throughout the section. However, taken as a whole, chlorite in argillites and highly argillaceous siltstones belongs to varieties with a roughly the same Mg^{2+} and Fe^{2+} ratio. The chlorite polytype $II\beta$ ($\beta = 97^{\circ}$) (Brown and Bailey, 1962) and Zvyagin's (1964) layer σ , as well as the insignificant on the whole and inconsistent addition of this mineral throughout the section, make it possible to assign the bulk of it to the authigenous variety that merely becomes more crystallized as the cation vacancies in its structure are filled up.

Kaolinite is present in rocks of the Lopatino and Vandady suites and to some extent in their analogs (Fig. 1, Samples II and III) and also in some sections of the Suktalma suite (Fig. 2, Sample II) in the Teya and Porozhnaya river basins. Kaolinite is most abundant in

*Electronographic study of clay minerals was made by B. B. Zvyagin, Z. V. Vrublevskaya, A. P. Zhukhlisov, and O. V. Sidorenko (Solodkova et al., 1975).

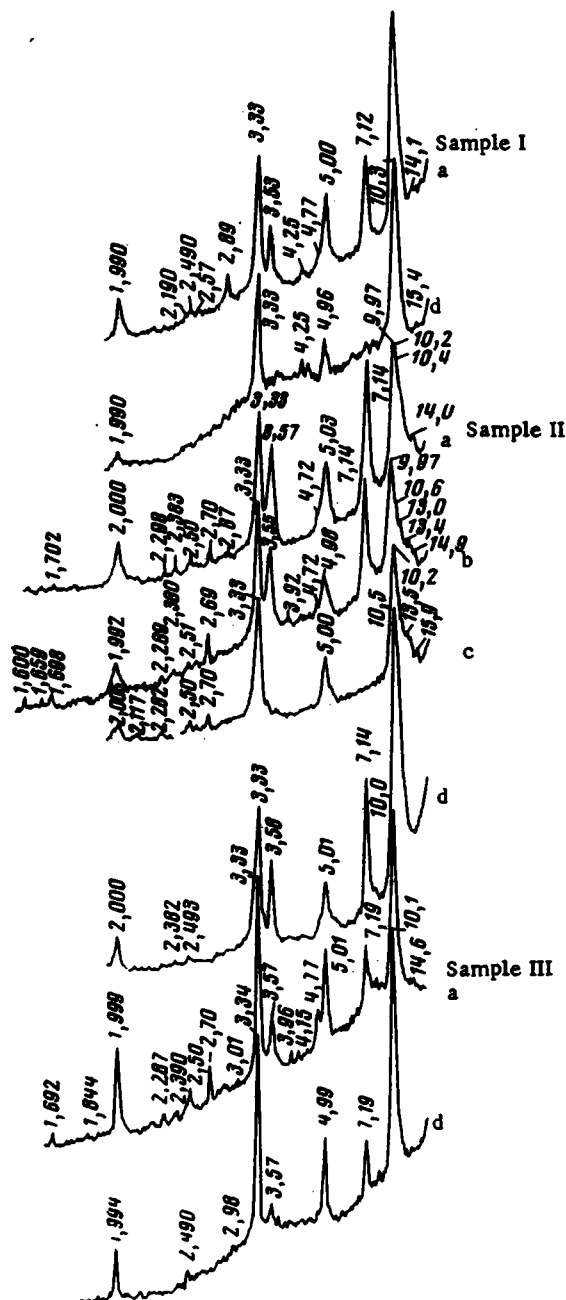


Fig. 1. Diffractometric curves for fractions <0.001 mm of Late Precambrian argillites and argillaceous siltstones in the Enisei Range, I) Chivida suite, mainly "tillites"; II) Vandady suite, black argillite; III) Lopatino suite, highly argillaceous red siltstone; a) original sample; b) ethylene-glycol saturated; c) heated for 2 h at 600°C ; d) treated with 10% solution of warm (80°C) HCl.

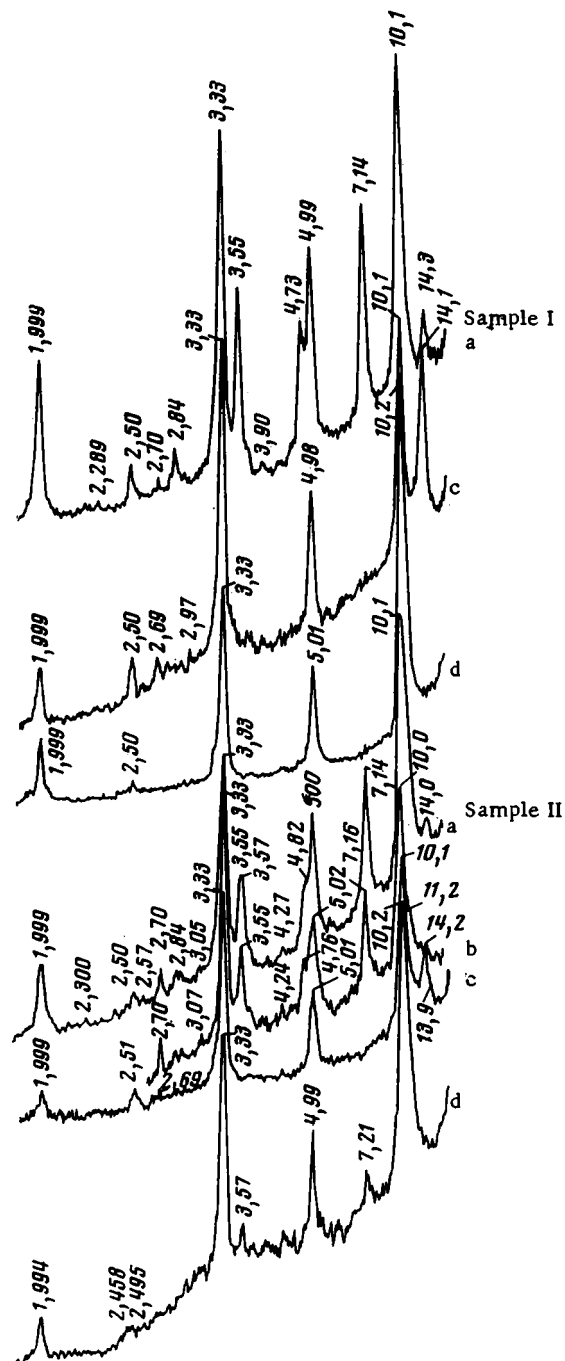


Fig. 2. Diffractometric curves for fraction <0.001 mm of Late Precambrian argillates in the Enisei Range: I) Nemchany suite of dark-red argillites; II) Suktalma suite of dark-red highly argillaceous siltstones. Symbols the same as in Fig. 1.

the Vandady series. Parameters of the kaolinite elementary cell are: $a = 5.16$; $b = 8.93$; $c = 7.13$ Å; and $\beta = 102^\circ$. The presence of kaolinite with slightly rounded crystallites (Fig. 3b) and of its typical microblocks (Fig. 3c), indicates its allothigenous origin (Solodkova and Kotel'nikov, 1971; Kotel'nikov and Solodkova, 1971, 1975).

In addition, montmorillonite is present in small amounts in tuff beds, 5-6 m thick, within the "tillite" section of the Chivida suite and its analogs, in northwestern and

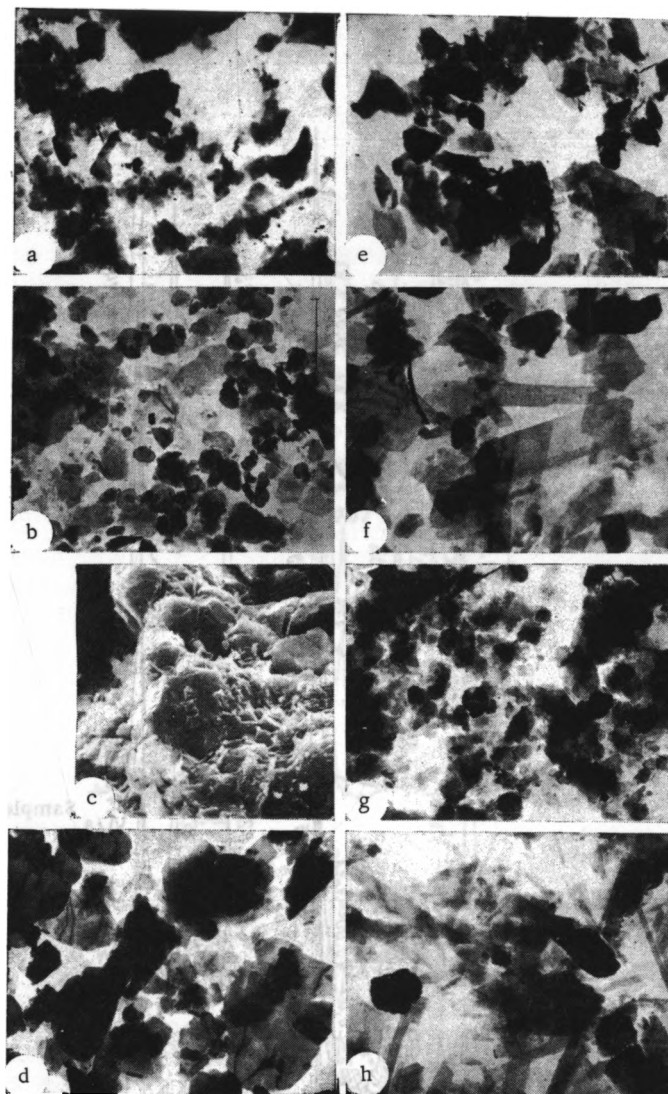


Fig. 3. Electron microphotographs of clay minerals in Late Precambrian rocks of the Enisei Range: a) Chivida suite, mainly "tillites," $\times 13,500$; b) Lopatino suite, red highly argillaceous siltstone, $\times 13,500$; c) Vandady suite, gray argillaceous siltstone, $\times 2000$; d) Vandady suite, blue-gray mixed-grain quartz sandstone, $\times 13,500$; e) Chivida suite, medium- to fine-grained tuffaceous sandstone, $\times 13,500$; f) Moshakovsk suite, dark-red fine-grained polymictic sandstone, $\times 13,500$; g) Moshakovsk suite, dark-red highly argillaceous siltstone, $\times 13,500$; h) Nemchany suite, dark-red arkosic coarse to medium-grained sandstone, $\times 13,500$; a, b, d-h) passing flow microscope (fractions <0.001 mm); c) scanning electron microscope (arbitrary chips of rock).

southern parts of the Enisei Range. In other parts of the section, the swelling component is present mainly in the mixed-layer montmorillonite-hydromica formation, where the ratio of nonswelling and swelling layers varies from 3:1 and 7:3 to 9:1, with a tendency for an orderly alternation of the components (Gradusov, 1971). Formations with the highest content of swelling layers are associated with rocks of the Vandady suite, while their content in the mixed-phase layer does not exceed 10% (see Fig. 1, Samples I and III; Fig. 2, Samples I and II).

Clay Minerals in Sand-Silt Rocks

In slightly clayey siltstones, and particularly in sandstones, the clay mineral associations are markedly different from those in argillites, both in composition and geometry (Fig. 3d-h), not only in different suites but also in parts of one and the same suite. Considering the development of strictly definitive varieties of clay minerals in such rocks, it is of great interest to determine the reasons for this association. For that purpose, we analyzed the features of clay minerals in sand-silt rocks in connection with their petrography and the character of the media of accumulation and subsequent transformation of allothigenous clay minerals and — what is most important — the origin of their authigenous varieties.

The predominantly quartz character of Lopatino sandstones and siltstones indicates a prolonged chemical weathering of the eroded source rocks on the continent, under humid conditions. The rock fragments (quartzites, mica schists, carbonate rocks) occur in them only in insignificant amounts. The feldspars are very rare. Other moderately to very unstable minerals occur sporadically. This suite is characterized by a high content of titaniferous hematite in its heavy fraction (intergrown with ilmenite and martite), in cement as well as in independent grains; leucoxene, octahedrite, and rutile also are present.

The coarse grain and poor sorting of clastic material indicate its accumulation in littoral parts of a shallow marine basin. Other evidence of that is the 0.015–0.027% boron content. Judging from a predominance of red beds in this section, the climate of that time was characterized by prolonged arid seasons during which iron — in contrast to reducing conditions of humid periods — lost its mobility and was deposited (Strakhov, 1960–1962). Oxidation conditions persisted also in the developed rocks. Their cement is a mixture of a mica mineral (close to sericite), variable amounts of kaolinite, and an insignificant admixture of chlorite (Fig. 4, Sample V).

Electron-microscopic study has shown that clay mineral particles are represented in argillaceous siltstones (Fig. 3b) and sandstones mainly by thin semitransparent pseudoisometric hydromica microblocks and by the more dense, slightly rounded pseudo-hexagonal kaolinite crystallites. The above-mentioned morphological features are known to be representative of allothigenous clay minerals (Methodological Manual..., 1957; Kotel'nikov, 1958, 1963, 1965). The elongated tablets of newly developed hydromica also are present in small numbers. The weak degradation of hydromicas in the presence of a relict admixture of chlorite, and a correspondingly small amount of kaolinite, suggests that climate in regions of denudation was on the whole not humid enough for a complete hydrolysis of primary minerals and for a significant removal of excess SiO_2 .

According to the electronographic data, the coarsest-grained sand-silt rocks of the Lopatino suite contain mainly hydromicas with parameters of the elementary cell: $a = 5.17$; $b = 8.96$; $c = 20.0 \text{ \AA}$; and $\beta = 96^\circ$; it belongs to polytype modification $2M_1$. Hydromica with parameters $a = 5.17$, $b = 8.96$, $c = 10.1 \text{ \AA}$, and $\beta = 101^\circ$ (polytype $1M$) is present as an additive.

The insignificant addition of authigenous hydromica in sand-silt rocks of this suite indicates a weak alkaline character (with a very low K^+ content) for the Lopatino basin. Correspondingly, considering the strongly weathered character of material coming in from the continent, viz., a practically complete decomposition of feldspars, clastic material, too, was low in K-minerals. That, in turn, led to a low content of this element in pore water. These mineral associations and morphological features of clay minerals are similar in this instance to basal sandstones of the Pashiisk suite we have studied in southeastern Tataria (Kotel'nikov, 1958).

Sand-silt rocks of the Vandady series consist largely of quartz with a small addition of quartzite and carbonate rock fragments, as the result of inflow into a marine (judging from the 0.011–0.032% boron content in rocks) basin of products much more strongly weathered than in the Lopatino time. Other evidence of that is the almost complete absence of unstable and partly stable minerals in rocks. The authigenous clay mineral associations in siltstones and particularly in sandstones are more diversified, with kaolinite in association with $1M$ hydromica and a small addition of the swelling component (Fig. 4, Sample IV) markedly predominant. Kaolinite is present mostly in variously rounded isometric to pseudoisometric microblocks with poorly preserved 120° angles (Fig. 3c). An addition of allothigenous kaolinite greater than in the Lopatino suite, in conjunction with a higher degree of hydromica

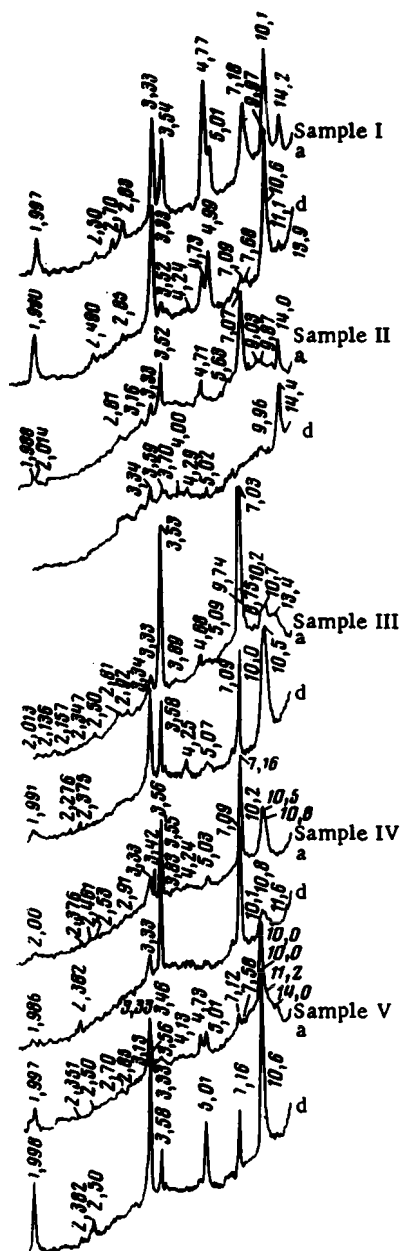


Fig. 4

Fig. 4. Diffractometric curves for fraction <0.001 mm of Late Precambrian sandstones in the Enisei Range: I) Moshakovsk suite, dark-red fine-grained polymictic sandstone; II) Chivida suite, dark-green medium- to fine-grained tuffaceous sandstone; III) Vandady suite, blue-gray mixed-grain quartz sandstone; IV) Vandady suite, light-gray fine-grained quartz sandstone with argillite stringers; V) Lopatino suite, dark-gray medium- to coarse-grained quartz sandstone. For symbols see Fig. 1.

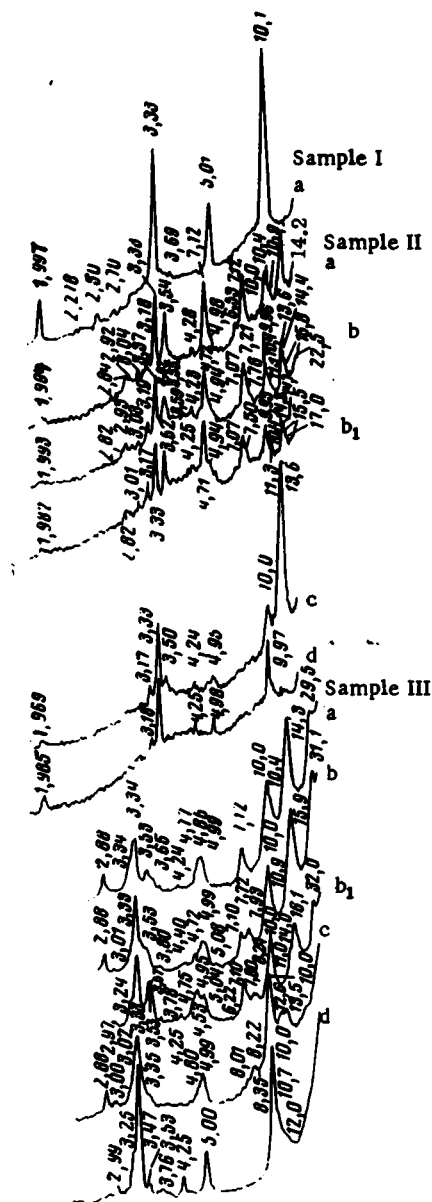


TABLE 1. Chemical Composition (%) of Fraction <0.001 mm in Sandstones and Siltstones of the Enisei Range and Northwestern Part of the Kansk-Taseevsk Trough

Sample Nos.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	P ₂ O ₅	Calc. loss	Total
78 ^b	47,3	0,38	23,80	6,75	2,50	0,12	5,15	0,65	N.d.	N.d.	N.d.	0,15	10,16	100,36
112	41,50	0,53	25,00	11,23	1,11	N.d.	6,51	0,26	0,08	4,28	1,20	N.d.	8,66	
116	45,0	0,70	22,40	12,80	1,78	»	6,02	1,20	N.d.	N.d.	N.d.	»	N.d.	
117	38,10	0,62	18,10	11,85	2,47	»	12,52	0,42	0,12	3,60	1,40	»	10,50	99,70
126	42,1	0,46	19,90	4,80	5,53	»	12,50	0,98	N.d.	N.d.	2,84	»	11,52	
95	52,40	1,70	16,58	2,25	8,59	»	7,60	0,48	2,00	0,90	N.d.	»	N.d.	99,65
165	46,8	0,96	18,40	5,35	10,32	»	6,60	1,96	N.d.	N.d.	»	»	»	
98	51,28	0,40	17,70	3,75	15,33	»	1,83	0,42	0,03	1,54	0,40	»	7,50	

Note. Sample 78^b) dark-red fine-grained arkosic sandstone from Nemchany suite, Teya-Chap synclino-
 rium, Enisei Range; 112) dark-red fine-grained polymictic sandstone from Moshakovsk suite, north-
 western part of the Kansk-Taseevsk trough; 116, 117) dark-red argillaceous siltstone, Moshakovsk
 suite, northwestern part of the Kansk-Taseevsk trough; 126) green-gray argillaceous siltstone from
 Chistyakov suite, northwestern part of the Kansk-Taseevsk suite (analog of the Chivida suite); 95)
 dark-gray medium- to fine-grained tuffaceous sandstone, Chivida suite, Teya-Chap synclino-
 rium, Enisei Range; 165) gray-green argillaceous siltstone, Sukhorechensk suite (analog of Chivida suite),
 Vorogovsk syclinorium, Enisei Range; 98) blue-gray mixed-grain quartz sandstone, Vandady suite, Teya-
 Chap synclino- rium, Enisei Range N.d.) Not determined.

degradation, also indicates accumulation of a more intensely weathered material in the Vandady time.

The predominantly gray color of sand-silt rocks, and the occasional presence among their authigenous minerals of a large number of pyrite pockets and crystals (in sandstones) and also dustlike accumulations of marcasite and occasional siderite concretions (in siltstones), indicate their deposition under moderately to strongly reducing conditions of the bottom layer. These conditions were replaced by the oxidizing only at the very end of the stage.

The principal component of cement in blue-gray mixed-grain quartz sandstones is a mineral with a two-stage structure — that of serpentine, to judge from changes in diffraction picture illustrated by diffraction curves following the processing of material (Fig. 4, Sample III), and from parameters of the elementary cell: $a = 5.36-5.37$; $b = 9.29-9.30$; $c = 7.05-7.20$ Å; and $\beta = 90^\circ$. The chemical composition of this mineral (Table 1, Sample 98) is characterized by a high ferrous iron content (15.33%) and a low magnesium oxide content (1.83%), which associates it with berthierite (ferruginous chamosite). In most instances berthierite belongs to structural type A + B, with a lack of regulation along axis b . At times, only the type A units are present in the mineral structure. Associated with this mineral in subordinate amounts is the polytype 1M hydromica and montmorillonite — a mixed layer hydromicaceous formation with the corresponding reflexes 10 Å and 10.7 Å. In addition, kaolinite (reflexes 7.09, 3.58, 2.375 Å) with a random structure, and occasionally chlorite (13.4 Å) consisting of type σ units (II_B , $\beta = 97^\circ$), are associated with it.

Berthierite is represented in electron microphotographs by well-expressed rosette crystallites (Fig. 3d), similar to those of hydromica particles present in sandstones and indicating their authigenous character.

Considering the high content of kaolinite in the enclosing argillaceous rocks, the origin of berthierite may be associated with solid-phase transformation of kaolinite in a strongly reducing medium with excess of ferrous oxide. Correspondingly, the content of elongated-tabular hydromica in these sandstones is quite insignificant, as it is in the Lopatino suite.

The Chivida sandstones and siltstones are markedly polymictic due to a low degree of decomposition of rocks eroded at that time on the continent, in a temperate but fairly humid climate. A short dry period occurred only at the end of this stage. Other evidence of a low-intensity chemical weathering of products brought in the Chivida basin is the presence in rocks, in addition to quartz, of plagioclases (often sideritized), K-feldspar, quartzite fragments, metamorphosed sandstones and siltstones, sericite-chlorite schists, and carbonate rocks. Also present are biotite leaflets, often chloritized; muscovite and chlorite scales; and fragments of intermediate composition effusives, often covered with a film of iron hydroxides. The fragments are mostly angular to semirounded, seldom slightly rounded, poorly sorted.

The sediments accumulated in a fairly deep marine basin (0.009-0.022% of boron in rocks) that became shallow by the end of that time. Reducing conditions prevailed in the bottom layer, thus ensuring a predominantly greenish color of rocks. The basin conditions became oxidizing only at the terminal stage of sedimentation.

The cement of tuffaceous sandstones in "tillites" of this suite is largely ferromagnesian chlorite with only a slight addition of hydromica (Fig. 4, Sample II). The electronographically obtained values of parameters of the elementary cell are: $a = 5.19$; $b = 8.98$; $c = 20.0$ Å; and $\beta = 95^\circ 40'$. Correspondingly, in connection with a substantial Mg^{2+} content in the structure of this chlorite (Table 1, Samples 95 and 165), parameters of its elementary cells are: $a = 5.32$; $b = 9.22$; $c = 14.5$ Å; and $\beta = 97^\circ 05'$, i.e., a and particularly b are slightly lower as compared with berthierites. As in argillaceous rocks throughout the Precambrian section of the Enisei Range, this chlorite belongs to the most stable polytype II_B ($\beta = 97^\circ$) or σ , although it obviously is authigenous in rocks under study and is associated with transformation of reactive primary volcanic material. Considering the very old age of the deposits, and especially their fairly significant alteration, the presence of subtype II_B in sandy and silty rocks may be associated in such instances (Hayes, 1970) with transition of the less stable polytype to a more stable one, as pressure and especially temperature increase (Bürost, 1969).

Seen under the electron microscope (Fig. 3e), chlorite particles usually are pseudoisometric; although larger than the hydromica microblocks, they are very thin (Sarkisyan and Kotel'nikov, 1971).

A consistent, although strictly subordinate, addition of chlorite, and a practically total absence of a swelling micaceous component in the "tillites," in conjunction with the presence of unstable to very unstable minerals in the heavy fraction, and of fresh feldspars in the lightweight fraction, likewise stress the low degree of chemical weathering of rocks in the source areas. In addition, these features of clay minerals indicate not only their preservation but also a progressive aggradation as compared to rocks of the Lopatino and Vandady suites — both in a marine basin with normal salinity at the sedimentation stage, and under conditions of a medium inherited in post-sedimentation alterations of subsequently developed rocks. The marked increase in chlorite content in argillaceous rocks of the upper part of the sequence (not counting the tuffaceous sandstones) indicates that the basin was somewhat isolated by the end of the Chivida time. As a consequence, Mg^{2+} of the volcanoclastic material, periodically brought in the sedimentation basin, concentrated in ooze water of the accumulating sediments, particularly in pore-filling solutions.

In the Suktalma time, rocks in some areas were weathered, in a warm and moderately humid climate, to the kaolinite stage. As a result, siltstones and sandstones of this suite, in areas of denudation of kaolinite products, consist mainly of quartz with a subordinate content of feldspatic material. Here, clastic material accumulated in a shallow-marine basin with a normal salinity and largely oxidizing conditions of the bottom layer.

In these rocks, clay minerals (Fig. 2, Sample II) contain mainly hydromica ($2M_1 + 1M$ in siltstones and $1M$ in sandstones), kaolinite, and also chlorite (II_B , $\beta = 97^\circ$).

Morphologically, clay mineral particles in sands and silts of the Suktalma suite are represented by a mixture of pseudoisometric and elongated tablets, with the latter much more numerous in the sandstones.

In the Stolbovaya River section, the Suktalma suite often contains stringers of green-gray polymictic sandstones. Their clastic fraction is represented by quartz, pelitized orthoclase, sandstones, siltstones, and ferruginous carbonates. The sandstones occur as lenticular stringers in dolomites. They accumulated in zones of higher mineralization of basin waters, with slightly reducing conditions in the bottom layer.

Present in these sandstones are regular mixed-layer chlorite-montmorillonite formations of the trioctahedral type, close to those systematized in the monograph of Sarkisyan and Kotel'nikov (1971) and subsequently described by Postnikova, Kotel'nikov, and Postnikov (1972), Krinari (1975), Kotel'nikov and Solodkova (1973), and Kossovskaya, Drits, Sakharov, and Sokolova (1975). As evidence of that, the diffractogram of the original sample (Fig. 5, Sample IIIa) shows a nearly integral-number series of reflexes, multiples of $29.5 \text{ \AA}$ (19.5 , 14.3 , 7.12 , 4.88 , 4.24 , $3.65 \text{ \AA}$). The Mg^{2+} -replaced sample swells when saturated either with ethylene glycol (Fig. 5, Sample III b) or, the most important, with glycerine. In the second instance, there originate series of reflexes, multiples of either $31.1 \text{ \AA}$ (31.1 , 15.9 , 7.72 , 5.08 , 4.40 , $3.80 \text{ \AA}$) or else $32.0 \text{ \AA}$ (32.0 , 16.1 , 7.80 , 4.53 , 3.78 , 3.57 , $3.24 \text{ \AA}$) following a calcination of the sample for 2 h at 550°C (Fig. 5, Sample IIIa). This feature is diagnostic of the presence of low-charge montmorillonite layers in the regular trioctahedral structures, as contrasted with high-charge vermiculite layers (Walker, 1958). A labile character of layers' interspace in this structure is stressed by a decrease in its period along axis c down to $24.2 \text{ \AA}$ (12.6 , 8.01 , 4.80 , $3.02 \text{ \AA}$) following a 2-h-long sample calcination at 550°C (Fig. 5, Sample IIIc). Correspondingly, the trioctahedral character of both types of layers is identified from a complete disappearance of the entire series of the regular mixed-layer phase following processing of the sample with a 10% solution of warm (80°C) HCl (Fig. 5, Sample IIId). Judging from parameters of the elementary cell in chlorite units of the mixed-layer phase in the basal plane ($a = 5.31$, $b = 9.20 \text{ \AA}$), their octahedral positions contain, similar to chlorite considered above, Mg^{2+} and Fe^{2+} . Associated with the mixed-layer chlorite-montmorillonite formation is hydromica $2M_1$ ($a = 5.22 \text{ \AA}$, $b = 9.02 \text{ \AA}$, $c = 20.1 \text{ \AA}$, $\beta = 96^\circ$) with an addition of trioctahedral chlorite and the montmorillonite-hydromica mixed-layer phase with a small amount ($<25\%$) of swelling layers.

The trioctahedral character of principal minerals in this association indicates that they contained deposits accumulated in basins close to the so-called evaporite type, at the initial stage of their development (Millo, 1968; Kossovskaya et al., 1975).

Sandstones and siltstones of the Nemchany suite vary in composition from more or less arkosic to pure quartz or polymictic. Their clastic fraction consists of quartz, K-feldspar, albite, oligoclase, microcrystalline schists, quartzites, sandstones, siltstones, and carbonate rocks. This indicates that, despite a warm and humid climate, only periodically becoming arid, physical weathering was predominant over the source area, largely because of a rapid removal of clastic material to the sedimentation basins. Hematite is present in large amounts both in the clastic fraction and in cement; it determines the predominantly red color of deposits. In the first half of Nemchany time, clastic material accumulated in an endemic marine basin and locally under lagunal conditions. The sea became shallow in the second half of that time, and the marine conditions gave place to lagunal-continental and continental.

Clay minerals in sandstones and siltstones of this suite are diversified in composition. Those in dark-red fine-grained varieties accumulated under reducing condition of the bottom layer, and characterized by a quartz-feldspar composition, are represented by hydromica 1M + 2M₁ in association with the dioctahedral chlorite-montmorillonite mixed-layer phase ($\alpha = 5.21$, $b = 9.03$, $c = 14.0$ Å, and $\beta = 96^\circ 30' - 97^\circ$), with a tendency for regulation (Fig. 5, Sample II; Table 1, Sample 78b).

Apart from that, the electron photograph shows a small addition of trioctahedral chlorite ($b = 9.18$ Å). In some instances, red sandstones similar in composition but coarser-grained, likewise accumulated under reducing conditions of the bottom layer, are cemented only by hydromica (Fig. 5, Sample I).

Under the electron microscope, this hydromica is of an elongated-tabular variety (Fig. 3h). Seen under the scanning electron microscope, the latter produces a latticed microstructure within the pores.

The Moshakovsk sandstones and siltstones are arkosic to polymictic (quartz, feldspars, fragments of quartzites, quartz-chlorite-sericite schists, less commonly of effusive rocks, hematite-cemented sandstones, and carbonate rocks), with the content of coarse-clastic material increasing going up the section. In the initial period, sediments accumulated in a shallow marine basin with a normal salinity and with oxidizing conditions of the bottom layer. The marine conditions subsequently gave place to littoral marine and then to lagunal-continental. The climate of that time was arid to semiarid, only occasionally becoming humid.

A distinctive feature of these sandstones was the presence of high-alumina chlorite in association with hydromica 1M + 2M₁. Chlorite of this type is expressed in diffractometric curves (Fig. 4, Sample Ia) by a series of reflexes, multiples of 14.2 Å, the most intensive being the 4.77-Å reflex. This chlorite is significantly more resistant to acid processing (Vlasov and Drits, 1964): its diffraction picture remains unchanged after a 2-h-long processing by 10% HCl at 80°C. It is affected to some extent only at a more intense HCl processing (Fig. 4, Sample Id). Even a 16-h-long processing achieves only a partial decomposition.

Judging from the electronographic data, this chlorite is of type σ (IIb, $\beta = 97^\circ$). The values $a = 5.21 - 5.22$ Å and $b = 9.02 - 9.03$ Å for its elementary cell are close to base parameters of its associated dioctahedral hydromica ($a = 5.17 - 5.21$ Å, $b = 8.97 - 9.02$ Å), very highly regular in this instance. The implication is that three-stage layers in the structure of this chlorite, in octahedral positions, contain largely Al³⁺ and possibly Fe³⁺ (Table 1, Samples 112, 116). In their turn, Mg²⁺ and Fe²⁺, along with part of Al³⁺, evidently are present largely in a single-stage layer. Consistent with these data, this chlorite can be assigned to the di-trioctahedral type (Eggleton and Bailey, 1967).

The electron microphotographs of samples with di-trioctahedral chlorite show elongated thin tablets characteristic of authigenous hydromica. Also present are even thinner wide strips. Because of their similarity in form to rectorite or alleverdite (Ivkin et al., 1970), they may be assigned to the di-trioctahedral variety of chlorite (Fig. 3f). Considering the geometry of particles of this chlorite, and its development in permeable rocks, it might be related to authigenous mineralization in pores of these rocks. The predominance of red beds in this part of the section indicates oxidation conditions for the bottom layer at the time of deposition.

The Moshakovsk red siltstones (with different content of clay material) also contain random mixed-layer chlorite-montmorillonite bodies of the dioctahedral type, in subordinate addition with hydromica and trioctahedral chlorite (Table 1, Samples 117, 126). In connection with the greater role of Mg²⁺ in chlorite structure, parameters a and b of its elementary cell are somewhat smaller ($a = 5.30$, $b = 9.18$, $c = 14.5$ Å, $\beta = 97^\circ - 97^\circ 10'$).

In the electron microphotograph (Fig. 3g), clay mineral particles are represented mainly by isometric tablets of hydromica with an addition of very thin pseudohexagonal crystals. In analogy with similar crystals of chlorite from Precambrian deposits of the Irkutsk amphitheater (Kotel'nikov and Florenskaya, 1973), these crystals, too, evidently belong to the chlorite-containing trioctahedral phase.

SUMMARY AND CONCLUSIONS

The data cited indicate that as the pH of the sedimentation medium, and oxidation-reduction potential of the bottom layer (Eh) change, either dioctahedral or di-trioctahedral and trioctahedral minerals of various types originate in sand-silt rocks of this section.

The authigenous dioctahedral clay minerals are represented by an elongated-tabular variety of micas. They developed in a broad pH range, from slightly acidic to alkaline (Rex, 1966) with a relatively high K^+ content in the medium (Methodological Manual..., 1957; Kotel'nikov, 1965), i.e., in open marine basins, with oxidation conditions of the bottom layer (interior part of shelf) being the optimum for their crystallization.

Genetically, the elongated-tabular hydromicas are one of the terminal members of a continuous series of three-stage minerals differing in dispersion of the elongated particles and, correspondingly, in their composition, primarily the K^+ content in the mineral structure (Kotel'nikov, 1965). The most dispersed varieties of this series have a low K^+ content (<3%) and a considerable amount of swelling layers, their number progressively decreasing as the dimensions of particles and the presence of K^+ in the structure increase. As a result, the elongated particles with their high dispersion are very close in composition and structure to montmorillonites and originate in an alkaline medium but with a relatively low K^+ content.

The micaceous layers increase in numbers as K^+ content in the medium increases together with its thermobaric parameters in the structure of elongated formations that adsorb Mg^{2+} from the aqueous medium, with its subsequent transition to octahedral positions and K^+ entry into the vacant positions. In this process, varieties with a relatively high K^+ content (of the order of 7-8%) acquire, in addition to the relatively large size of their particles, sphenoid angles of 120° (Kotel'nikov, 1965; Sarkisyan and Kotel'nikov, 1971). Beutelspracher and Van der Marel (1968) proposed to name this variety of hydromica, sarospatakite, after a locality in Hungary. However, inasmuch as this variety is but a member of a continuous series of minerals, we do not believe it expedient to single out with a special name any of its members, even the terminal. As we have observed, each such member develops under definite thermobaric conditions, consistent with the general order of aggradation of swelling minerals in sedimentary rocks in the process of subsidence with the attendant rise in geostatic pressure and, even more importantly, in temperature (Bürost, 1969). This process is intensified by deformation of deposits: under high stresses and at high temperatures, the primary swelling structures are modified to a greater extent, up to complete contraction of all the interspaces between the layers.

The implication is that a widespread development of elongated-tabular hydromicas solely in the upper part of the Late Precambrian section, beginning with the Suktalma and Moshakovsk suites, indicates that sedimentation at the earliest stages of that time proceeded in a medium highly deficient in K^+ .

In contrast to the three-stage dioctahedral structures whose octahedral positions are occupied by trivalent cations, mainly Al^{3+} , Fe^{3+} , etc., the same positions in similar trioctahedral structures are occupied by bivalent cations, mainly Mg^{2+} and Fe^{2+} . Therefore, emergence of trioctahedral structures at various stages of postsedimentation rock alteration necessitates primarily the presence of adequate amounts of bivalent Fe cations in the mineralization medium, i.e., reducing conditions. In the joint presence of bi- or trivalent cations, and depending on their ratio, different minerals evidently can originate, beginning with di- and di-trioctahedral and up to trioctahedral varieties strictly speaking.

Thus, a relatively low Mg^{2+} content in the sedimentation medium leads to development, at the epigenesis (catagenesis) stage, of dioctahedral mixed-layer chlorite-montmorillonite or else of di-trioctahedral chlorites, such as in some sandy stringers in the Nemchany and Moshakovsk suites. Emergence of the swelling or nonswelling phase evidently is controlled by the intensity of primary swelling dioctahedral material with different charges of the tetrahedral lattices (Frank-Kamenetskii and Kotov, 1975). Such conditions obtain in a weak

hydrothermal alteration of permeable rocks. In our instance, this means largely development of a brucitelike layer in interspaces between layers in the structure of the original minerals. In the beginning, these layers originate only between the tetrahedral lattices with a higher negative charge (chlorite-montmorillonite); then they spread to the remaining interspaces (di-trioctahedral chlorite). In this process, the composition of three-stage dioctahedral layers changes but very little.

The trioctahedral chlorite-montmorillonites develop in the medium with a high Mg^{2+} content (Kossovskaya, 1966). Judging from the available data, regular trioctahedral mixed-layer chlorite-montmorillonite formations are present in deposits of different ages, occurring at great depths. They associate here with a mixed-layer montmorillonite-hydromica phase with different numbers of swelling layers. This indicates that they develop and, what is most important, remain stable within a broad range of thermobaric parameters of the medium — because of a stronger bond with water in their structure, as compared with the dioctahedral minerals (Postnikova et al., 1972; Sarkisyan and Kotel'nikov, 1972; Kotel'nikov et al., 1976).

According to Viar and Sabatier (1969), chlorite-montmorillonites may originate out of montmorillonite or hydromica. These authors state that, in the instance of montmorillonite character of the original material, Mg^{2+} may be present in the mineralization medium as the product of $MgCO_3$ dissociation.

As implied by the Viar and Sabatier scheme (1969), origin of trioctahedral chlorites strictly speaking is related to a more intensive transformation of the primary swelling structures. Magnesial-ferruginous and ferruginous-magnesial chlorite, the most common in epigenetic (catagenetic) alterations of rocks, are characterized by the presence in their structure not only of Mg^{2+} but also of Al^{3+} and a considerable amount of Fe^{2+} .

Berthierites, like serpentinite proper, are 7-Å-trioctahedral layered hydrosilicates. Depending on the cation of the mineralization medium, a 7-Å mineral of different composition may develop. Namely, reducing conditions typical of some Vandady sedimentation stages, and the presence of considerable amounts of hematite in contemporaneous deposits of the Aleshinsk suite, evidently were responsible for a very considerable iron content. The total effect was development of ferruginous layered silicates of the chamosite type.

Thus, the main factor controlling development of a certain type of authigenous clay minerals is chemism of the medium, determined both by the character of material coming into the basin and the sedimentation conditions of the latter. Material coming in during the early sedimentation stages is, as a rule, strongly weathered, inert, represented largely by quartz, while the medium is deficient in cations. That determines a continuation of degradation for clay minerals not only in sedimentogenesis but also at early postsedimentation stages. As a result, the allothigenous varieties of dioctahedral clay minerals (kaolinite, hydromica, montmorillonite) develop at this stage of basin development. Correspondingly, postsedimentation clay development in permeable rocks, as well as development of the elongated-tabular variety of dioctahedral hydromica and trioctahedral chlorite, proceeds on a limited scale. The material coming in at stages of regressive sedimentation is but slightly decomposed, while the medium is characterized by a high content of cations, because of a shrinking and even partial isolation of the basin. As a result, beginning with the sedimentogenesis stage and up to the metagenesis, allothigenous clay minerals are aggraded, while postsedimentation alterations of permeable rocks bring about a significant development of authigenous clay minerals. Various trioctahedral minerals, including chlorite-montmorillonite, develop at the early stage of rock alteration, in a high Mg^{2+} medium, under reducing conditions ensuring the presence of bivalent iron. The three-stage dioctahedral minerals of the elongated-tabular hydromica type develop at the late alteration stage. In their turn, dioctahedral chlorite-montmorillonite and di-trioctahedral chlorites develop under intermediate conditions characterized by the presence of Mg^{2+} in the medium, necessary for development of brucitelike layers, on the one hand; and under reducing conditions a stable maintenance of Fe^{2+} in octahedral positions of the original dioctahedral minerals, on the other.

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MAGNESITE ORE OF THE SAVINA DEPOSIT

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UDC 553.682(57.2)

The geological features and origin of the Savina magnesite ore, and its structural position in the East Sayan area, are described. Six types of magnesites are recognized in this deposit according to textural features: 1) banded medium-grained and brecciated; 2) fine-grained; 3) medium-grained marbly; 4) "stellate"; 5) columnar and rod-shaped; and 6) very coarsely crystalline. These are combined into three ore groups, which have definite spatial distributions. Patterns of variation in magnesite quality established for these textural types are related to the stage of magnesian apocarbonate metasomatism.

The Savina magnesite deposit located in East Sayan is the largest such deposit not only in the Soviet Union but in the world.

The deposit is limited to the Onot graben of the East Sayan area. This graben is a major proterozoic north-south-trending synclinal structure superimposed on the older Archean Sharyzhalgai projection of the Siberian Platform (Shames, 1962). Of the greatest interest is the southwest part of the Onot graben, where the Onot-Savina group of deposits of talc (Onot), magnesite (Savina, Onot), and iron ore (Sosnovyi Baits, Biboi, and others) are restricted to the Lower Proterozoic Kamchadal' and Sosnovyi Baits suites. The location of the deposits is controlled by the deep Alagin fracture zone, along which magmatic and metasomatic process have been active.

The main results of a study of the features of the magnesite ore, carried out by the author during detailed examinations of the deposit in 1961-1967, are presented herein.

Irkutsk Geological Survey, Ministry of Geology of the USSR, Irkutsk. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 85-98, November-December, 1977. Original article submitted May 12, 1977.

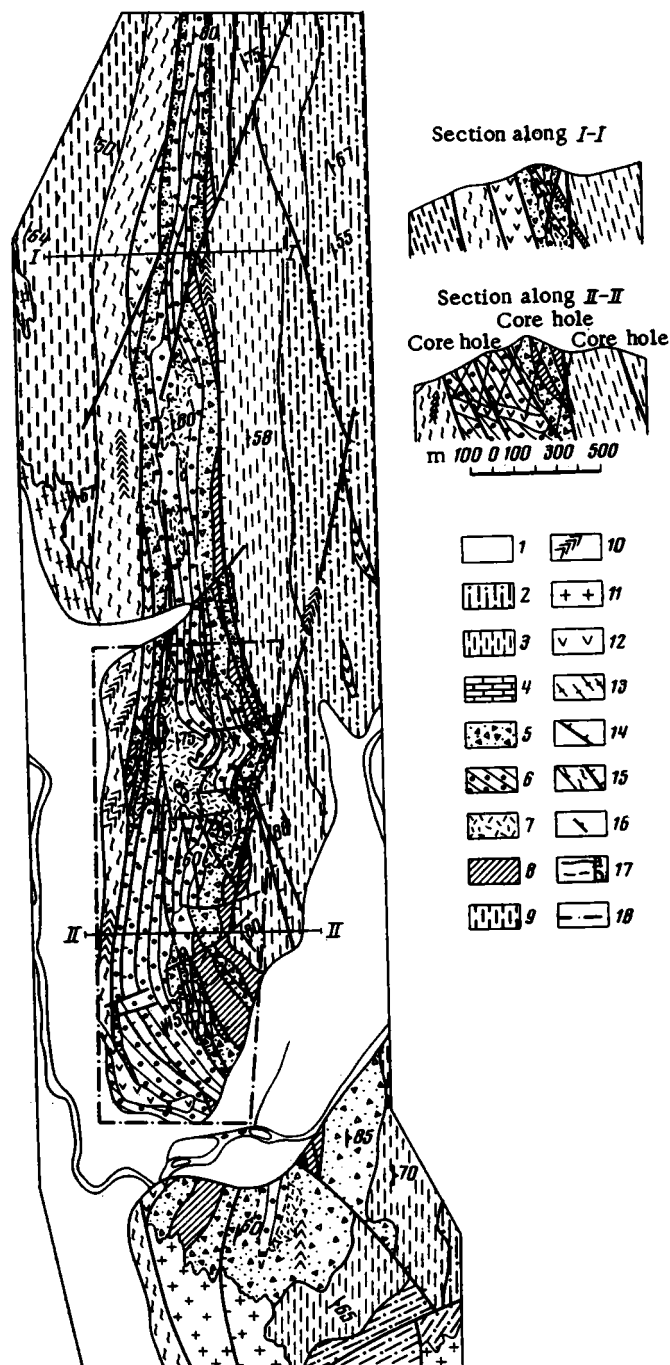


Fig. 1. Geologic map of the Savina deposit. 1) Cenozoic alluvium. Lower Proterozoic units of the Kamchadal and Burukhtui suites (2-9): 2) biotite, garnet-biotite, biotite-amphibole, chlorite, and carbonate schists; 3) interbedded talc-chlorite-serpentine and carbonate schists and dolomite with magnesite lenses; 4) dolomite with lenses of talc-chlorite-serpentine rocks. Areas of predominant development of magnesite (5-7): 5) brecciated and banded textures; 6) "stellate" textures; 7) columnar and very coarsely crystalline textures; 8) horizon of amphibolites and chlorite-serpentine schists; 9) biotite-amphibole microgneiss with interbeds of biotite and pyroxene-biotite amphibolite and marble. Intrusive units: 10) Upper Proterozoic Nersinsk diabase and dolerite complex; 11) Middle Proterozoic Savan biotite and amphibole-biotite granite and granodiorite complex; 12) Middle Proterozoic Arbansk gabbro-diabase and orthoamphibolite complex; 13) Lower Proterozoic Onot gneiss-granite complex; 14) tectonic disruptions; 15) diaphthorite and cataclasite zones; 16) elements of bedrock structure; 17) boundaries of occurrence of various textural types of magnesite: a) established, b) proposed; 18) boundary of detailed exploration of the deposit.

The Savina deposit is in the southeast part of the Onot-Savina group and lies within the thick, so-called productive horizon of the carbonate rocks of the Kamchadal suite. The magnesite forms a steeply dipping deposit extending 9 km from northwest to southeast, with an outcrop width ranging from 100 m at the ends to 600 m in the center. The deposit is in contact with a zone of mylonite and diaphthorite of the Nizhne-Biboi fault on the southwest, and is bordered on the northeast by a system of en echelon wrench faults along an amphibolite horizon of the Kamchadal suite. Later, upon formation of the ore deposit, there was an unusual gradational boundary of development of the processes of apocarbonate magnesium metasomatism. To the northwest of the deposit the magnesite is tectonically cut off, and to the southeast it ends in a granitoid massif of the Middle Proterozoic Sayan' intrusive complex (Fig. 1). The depth of the magnesite occurrence has not been established. Two core holes 700 and 780 m deep within the deposit failed to pass through the magnesite (Poletaev et al., 1975).

The Kamchadal suite is divided into two parts in the deposit: a lower, essentially carbonate, and an upper, carbonate-terrigenous. The suite is subdivided into several horizons (from the base upward):

1. Magnesite with relict dolomite, dolomitic marble, and sparse talc-chlorite-serpentine interbeds. Thickness more than 600 m.
2. Fine-grained gneissic amphibolite and talc-serpentine-chlorite schist. Thickness 80-100 m.
3. Dolomite and dolomitic schists with lenses of magnesite and talc-chlorite-serpentine rocks. Thickness 120-170 m.
4. Rhythmically interstratified biotite, biotite-amphibole, garnet-biotite, chlorite, and carbonate (dolomitic) schists. Thickness more than 200 m.

One of the most characteristic geological features of the Savina deposit is the widespread, almost ubiquitous presence of metasomatism. The metasomatic rocks are divided into two basic groups: apocarbonate and apocaluminosilicate. The apocarbonate metasomatites include rocks containing magnesite, ankerite, stilpnomelane and calcite, and talc, and pyritic rocks with associated talc, chlorite, quartz, and dolomite, and magnetitic serpentinites. The apocaluminosilicate group includes talc-chlorite-serpentine schists and chlorite-serpentine rocks containing abundant quartz veins.

Intrusive rocks in the region of the Savina deposit were emplaced during three main tectonic-magmatic stages of the Proterozoic.

The oldest igneous rocks in the Onot graben are orthoamphibolites of the Urda-Okina complex and granite gneisses of the Onot complex of Lower Proterozoic age. They are found on the western flank of the deposit, beyond the magnesite area. Regional metamorphism, migmatization, and granitization are related to the intrusion of the Onot granitoids in the graben, and in its final stages, alkaline (potassic) metasomatism in acidic aluminosilicate environments, and in the author's view, magnesium metasomatism in carbonate and basic rocks in areas of deep faulting.

A Middle Proterozoic tectonic-magmatic stage in the deposit is represented by the Arban basic intrusive complex and by granitoids of the batholith of the Sayan' intrusive complex. The Arban complex includes orthoamphibolites, with gabbro-diabase relicts, occurring in dikes. In the northeastern part of the deposit they are thin, steeply dipping dikes of limited extent, while in the central part (the belt of apocarbonate magnesites) they are gently dipping bodies of variable thickness (10-100 m) and extent. The largest (60-100 m thick) of these gently dipping orthoamphibolite dikes cuts across the magnesite deposit at a depth of 150-300 m. This dike has been traced for a distance of more than 5 km. To the southwest the dike is restricted by a zone of diaphthorites of the Nizhni-Biboi branch of the Alagnin fault, and to the northeast there is a blunt "bulbous" pinchout 300-400-m down dip. Several other gently dipping thin (up to 10 m) bodies of basic rocks of the Arban complex lie above and below it.

In the exocontact zones of the basic rocks sizeable deposits of pyrite and talc or pyrite, dolomite, and quartz are found within the magnesites as a result of metasomatic processes of the contact-infiltration type (Nadelyaev, 1956; Poletaev and Ivanov, 1971).

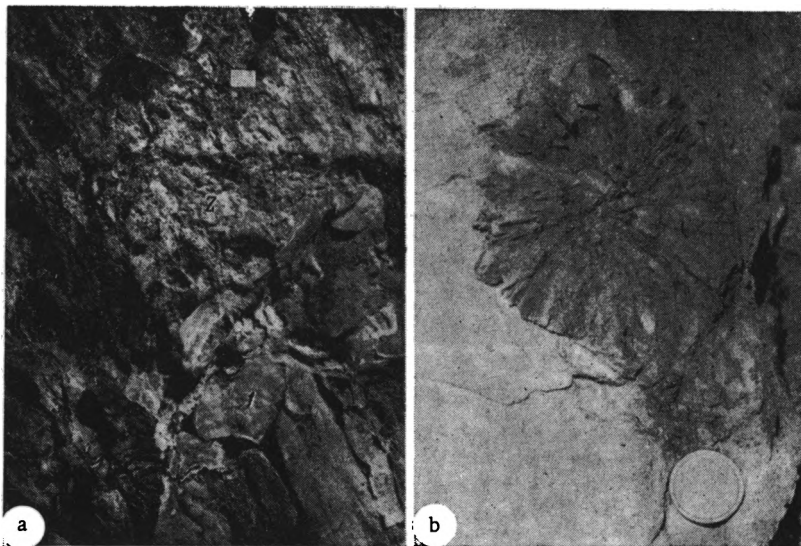


Fig. 2. Replacement of dolomite (1) by magnesites (2) in the Kamchadal suite: a) along a fracture system and across platy bedding; b) "stellate" crystal groups of magnesite in dolomite.

Granitoids of the Sayan intrusive complex, which lie on the southeast flank of the Savina ore field, have not been exposed to magnesian metasomatism. Therefore, this complex is considered by the authors to be a deep magma chamber, a source of heat and solutions that produced additional metamorphic and metasomatic effects on rocks located in the ore deposit.

The final stage of Proterozoic magmatism was expressed in the introduction of numerous diabase dikes and diabase porphyries of the Upper Proterozoic Nersinsk intrusive complex.

Structurally, the deposit is on a northwest-trending monocline ($320-340^\circ$) with a north-east dip ($40-90^\circ$). The monocline is complicated by a series of rather large flexures and folds of a higher degree that are nearly isoclinal. Observation of the interrelationship between the folding, on the one hand, and intrusion and metasomatism, on the other, leads to the conclusion that at least two stages of folding have affected the structure of the ore deposit. A principal role in the structural development of the deposit is assigned to disjunctive vertical dislocation, which created a complex system of fault blocks within the ore field.

Main Features of the Magnesites

Numerous field observations and petrographic studies indicate that the magnesites of the Savina deposit are metasomatic apodolomitic. Nadelyaev and Smolin (1958) arrived at the same conclusion.

The metasomatic origin of the magnesites is indicated by the following basic factors.

1. The presence of large amounts of relict primary sedimentary dolomites within the magnesites, contacts with which are corroded, sharp, and frequently cross-cutting the original bedding.

2. Magnesites of the ferrous type and isolated groups of magnesite crystals developed along fractures are found in dolomite sequences in tectonic zones (Fig. 2).

3. Thin sections reveal the replacement of fine grains of dolomite by rod-shaped or rhombic magnesite crystals in which dolomite that has not been completely replaced, clinochlore, and even talc are sometimes preserved.

4. The presence of large lenticular bodies of metasomatic rock composed of stilpnomelane-calcite and ankerite, related to tectonic dislocations, in originally dolomitic rocks of the Kamchadal suite.

5. Paleothermal calculations indicate that magnesite crystallization took place at temperatures no lower than $240-280^\circ\text{C}$.

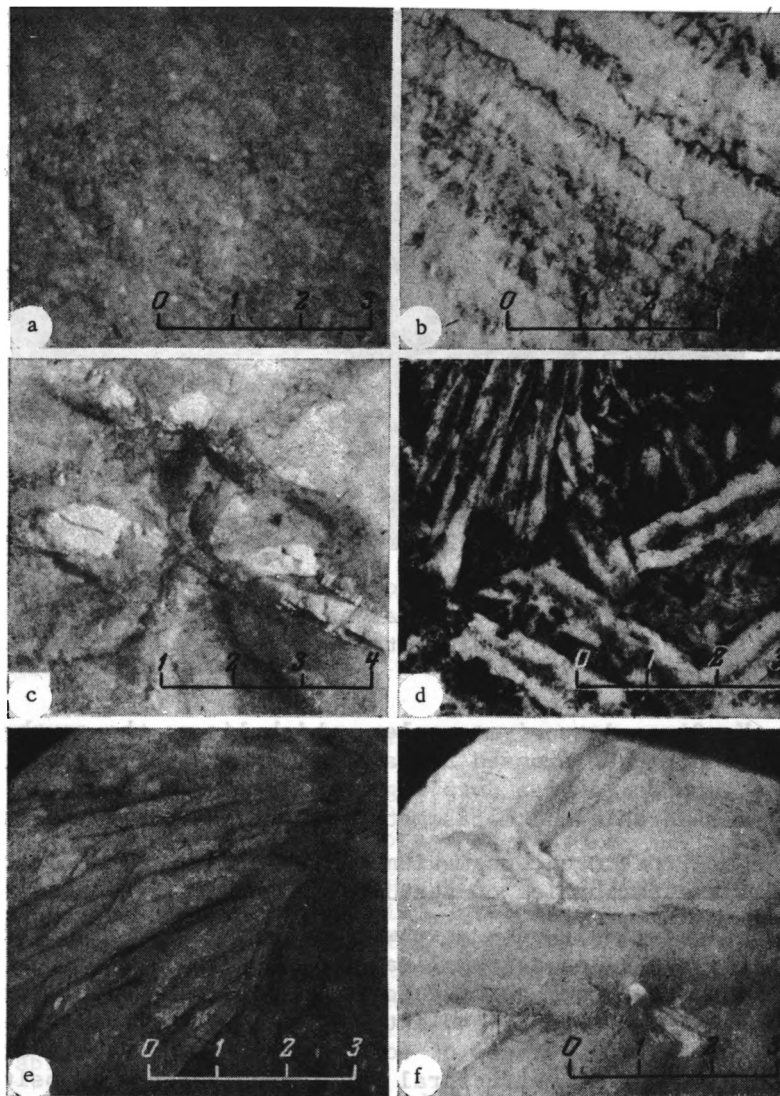


Fig. 3. Textural types of magnesite ores in the Savina deposit: a) fine-grained marbly; b) banded marbly; c) "stellate"; d) brecciated; e) columnar; f) very coarsely crystalline.

The magnesites of the Savina deposit are quite complex in their internal make-up and are represented by several clearly outlined areas of magnesites of various textural types (or combinations of types) among which the following are recognized (see Fig. 3).

a) Fine-grained, blue to bluish-white, coarsely foliated, visually indistinguishable from dolomite. The texture is equigranular (grain size 0.3×0.5 to 0.4×0.7 mm), granoblastic.

b) Marbly, massive or coarsely foliated (to banded), light gray and light-blue, medium grained, with a heterogranoblastic groundmass, locally changing to lepidogranoblastic on account of inclusions of chlorite and talc, developed along the foliation. In the latter case the magnesite acquires an indistinct banded texture. The magnesite grains have a rhombohedral habit usually with irregular, gently undulating outlines, and are randomly located with an indistinctly expressed orientation. Grain size from 0.5×0.7 to 3.0×4.0 mm.

c) Coarsely crystalline with short prisms on the long axis, very often with large spherical groups of crystals with a radial "stellate" texture. These "stars" reach 10 to 12 cm in diameter. They are light gray to white with barely discernible light blue shades. The size of the crystals is from 3.0×5.0 to $7.0-10.0 \times 25$ mm.

d) Brecciated coarsely crystalline, composed of 80-85% magnesite crystals and 15-20% talc and chlorite. The magnesite crystals have an elongated rhombohedral habit and straight edges, and are 3-5 to 6-7 cm across. The rock is massive, with talc and chlorite forming branching zones at the contacts of the crystals or cutting across them along numerous fractures. In the coarse, thickly grown crystals of brecciated magnesite inclusions of semi-dissolved fine rhombohedral grains of magnesite and dolomite are often found. Banded magnesites, which differ from the brecciated by their medium-grained crystals of magnesite and banded texture caused by an alternation of bands made up of crystals of light-gray magnesite with bands of dark-gray talc-chlorite material, are found in close association with the brecciated.

e) Coarsely crystalline light-colored magnesites with a rodlike or columnar texture, composed of columnar crystals, oriented across the foliation, that are up to 10 cm on the long axis and up to 0.5-1.0 cm along a rhombohedral diagonal. Fine veinlike magnesite bodies of "rosettelike" form and radial structures with chalcedonic quartz in the center are sometimes found among them.

f) Very coarsely crystalline, pure white magnesite with clearly expressed rhombohedral crystals 10-20 cm across.

The following patterns are observed in the spatial distribution of the textural types of magnesite ore.

I. The first three types of magnesite occupy almost the entire southern part of the ore deposit. In the central part (in the flexure zone) these give way to columnar and rod-shaped magnesites and are found as small (20 × 60 m in size) irregularly shaped bodies, while in the north they are in relatively large bodies elongated along strike (up to 100 m thick and 700 m long) adjoining areas of basic dikes and near the edge of the occurrence (see Fig. 1).

II. Magnesites of the fourth type (brecciated, banded) form the hanging wall and to a lesser extent the footwall of the magnesite deposit, making an elongated, concordant zone up to 100 m thick for the entire length of the deposit. They are almost gone in the central part. Narrow, elongate bodies (3-60 m thick) along tectonic sutures and the hanging wall of the deposits are exceptions. A large number of interbeds and lenses of the banded, medium-grained varieties are noted among the brecciated magnesites.

III. Rod-shaped, columnar, and very coarsely crystalline magnesites (fifth and sixth types, Fig. 3e and f) are sharply set apart among the rest of the magnesite types. They occur in a large area (400 × 600 m) in the center of the deposit, in the flexure zone, where the amphibolite horizon overlying the magnesite deposit is cut by a tectonic disturbance. In the southern and northern parts of the deposit these magnesites are relatively rarely found as elongate lenses and veinlike bodies (up to 20-30 m thick and 400 m long), restricted to tectonic disturbances, highly faulted zones, and other areas of weakness from tectonic strain (see Fig. 1).

A study of the nature of the relationships between the various types of magnesite ore and country rock shows that the formation of magnesite can be divided into two stages, corresponding to the two periods of magnesium metasomatism. The first stage is indicated by the marbly, "stellate," and brecciated textures. The replacement of dolomites by fine- and medium-grained magnesites, which are in turn replaced by the coarser crystalline "stellate" types, can be clearly seen in hand specimens and thin sections. First noted in the dolomites and fine-grained magnesites are individual "stellate" forms of groups of short, stubby magnesite crystals, the number of which gradually increases until the magnesite rock becomes coarse grained. Similar interrelationships are also found between the banded marbly and brecciated varieties in the hanging wall of the deposit.

The writers assign to the second stage the formation of magnesites of columnar and rod-shaped texture, the formation of which apparently takes place not only under the effect of recrystallization processes, but also by an additional supply of new magnesite solutions.

There is a considerable time interval between the formation of the various textural types of magnesite (marbly, "stellate," brecciated, rod-shaped, and columnar-fibrous). This is indicated by: 1) the sharp reaction contacts between rod-shaped and columnar magnesite bodies and magnesites of the other types; 2) the association of columnar and rod-shaped magnesites with structural elements occurring over the principal structural features (tec-

tonic disturbances, folds); 3) the appearance of chloritization, talcization, and pyritization between the formation of "stellate" and brecciated magnesites, on the one hand, and columnar on the other, according to petrographic studies; 4) differences in the chemical composition and chrome content, which does not exceed 3-5 g/ton in the groundmass but reaches 20 g/ton in columnar and rod-shaped magnesites (from spectral analyses of 23 samples). No differences have been established between the known textural types in any of the other minor elements (Ca, Ni, Mn, P, V, etc.).

Thus, two major stages in the formation of metamagnesites can be proposed, and consequently, two stages in the magnesium metasomatism of the Savina deposit, and possibly even in the entire belt of the Onot-Savina group of deposits. The first stage in the formation of magnesite can be considered the basis for the magnesium apocarbonate metasomatism, while the formation of rod-shaped and fibrous magnesites are probably the result of recrystallization along zones of tectonic weakness with the introduction of new dolomitic blocks of the Kamchadal suite into the replacement zone. During the stage of magnesium metasomatism, basic dikes of the Middle Proterozoic Arban complex were intruded. Replacement processes (chloritization and serpentization took place in these rocks only in zones of tectonic disruption along which the rod-shaped and columnar magnesites were also developed. Two stages of magnesium metasomatism are also seen in aluminosilicate rocks of the Kamchadal suite (amphibolites, chlorite-serpentine associations, talc-chlorite associations), which is borne out by calculations according to the Barth method carried out by Poletaev and Ivanov (1971).

The magnesites in the deposit represent a nearly monomineralic rock, made up of 75-99% magnesite. The undesirable minerals forming 1-25% of the rock are relicts of the original fine-grained dolomite, talc, chlorite, quartz, pyrite, coarsely crystalline hydrothermal dolomite, etc.

Relicts of the original dolomite are found predominantly in areas where fine-grained marbly and coarsely crystalline "stellate" magnesite are developed (the southern part of the deposit). These are in small elongated lenses several centimeters to 10-20 m thick and 5-10 to 30-35 m long. These are essentially absent in columnar magnesite.

Talc-chlorite inclusions are found in magnesite as thin veins 3-40 mm thick, small filmlike selvages along fractures, and clusters from a few mm to 2-3 cm in size. In rare cases they form relatively large lenses and veins up to 1-2 m thick and 5-8 m long. The degree of impregnation of magnesites by talc and chlorite is quite uneven. In areas of tectonic sutures and zones of intensive fracturing the amount of talc and chlorite reaches 3-20%, and decreases away from them to 0.5-1%. In the deposit, as a whole, a clear-cut pattern in the distribution of talc and chlorite is seen, which consists of a gradual increase in amount from the center of the deposit to its eastern and western margins. The banded and brecciated magnesites most "contaminated" by talc and chlorite (and locally also by serpentine) are in the eastern part of the deposit, where they amount to 10-25% of the total rock. This situation can be partially explained by analysis of the composition of the original dolomite of the Kamchadal suite. Dolomites of the relicts preserved in the central part of the deposit have a relatively pure chemical composition (MgO, 23.51%; CaO, 27.66%; SiO₂, 0.24%; R₂O₃, 0.84%; ignition loss, 45.28%; average of 45 analyses), while dolomites of the eastern edge of the deposit are considerably enriched in silica, iron, aluminum, and other elements (MgO, 21.4%; CaO, 25.5%; SiO₂, 7.65%; R₂O₃, 2.52%; ignition loss, 41.90%; average of 32 analyses). Moreover, talcization and chloritization are more intensively developed in exocontact zones of basic rocks, which are associated with contact-infiltration and diffusion metasomatism at the boundaries of the chemically contrasting bodies. The lowest talc and chlorite content was found in columnar magnesites.

Quartz in the magnesite forms pockets and veins filling fractures, and in very rare cases, small drusy vugs of transparent crystals 3-4 cm in size. It is most frequently associated with coarsely crystalline low-temperature hydrothermal dolomite.

Pyrite is found nearly everywhere in the magnesite as fine disseminated grains, barely visible to the naked eye (0.1-1.0%). A sharp increase in content is noticed in zones of tectonic sutures, increased fracturing, and in exocontact areas of dikes and concordant basic rocks. It is interesting that upon formation of columnar magnesite some enrichment in pyrite took place along its contacts with marbly and "stellate" magnesites. Among other extraneous material in magnesite should be mentioned veins of serpentinite with magnetite and asbestos.

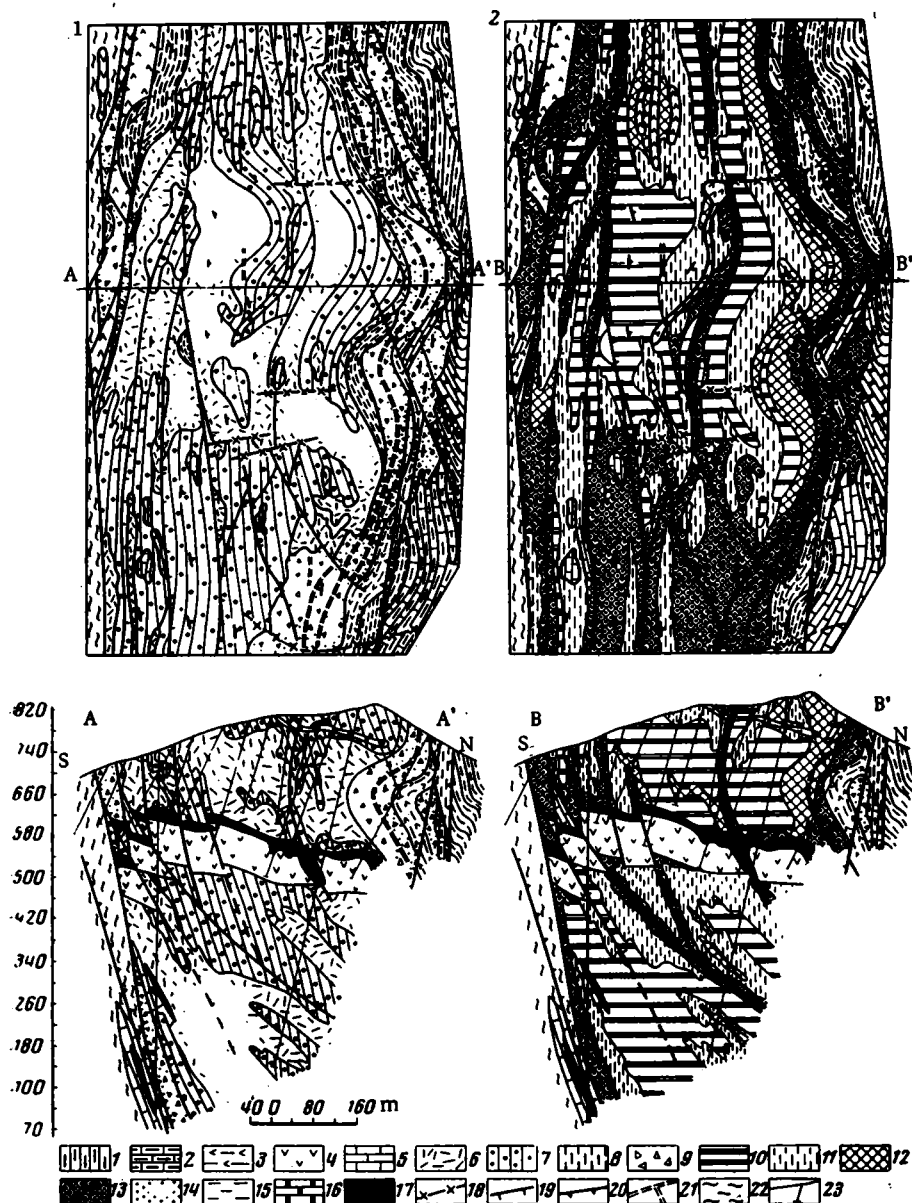


Fig. 4. Geological (1) and ore quality (2) maps and sections (A-A' and B-B') of the central part of the Savina deposit (prepared by A. F. Shcherbakov): 1) biotite, garnet-biotite, biotite-amphibole, chlorite, and carbonate schists; 2) recrystallized dolomites; 3) gneissic amphibolite and chlorite-serpentine schists; 4) amphibolitic gabbro-diabase and orthoamphibole; 5) relict original dolomite. Areas of predominance of magnesite textures: 6) columnar, rod-shaped and very coarsely crystalline; 7) fine- and medium-grained and "stellate"; 8) banded; 9) brecciated. Areas of predominance of magnesite by grade: 10) first and second grade; 11) third grade; 12) fourth grade; 13) substandard (SS); 14) pyritized zone; 15) interbedded talc-chlorite-serpentine and carbonate schists and dolomites with magnesite lenses; 16) ankeritic and stilpnomelane-calcitic rocks; 17) chlorite-serpentine rocks. Faulting: 18) nearly east-west, post-ore; 19) nearly north-south, mineralized, post-ore; 20) concurrent with ore; 21) intensive fracture zones; 22) diaphthorite and cataclasite zone; 23) core hole.

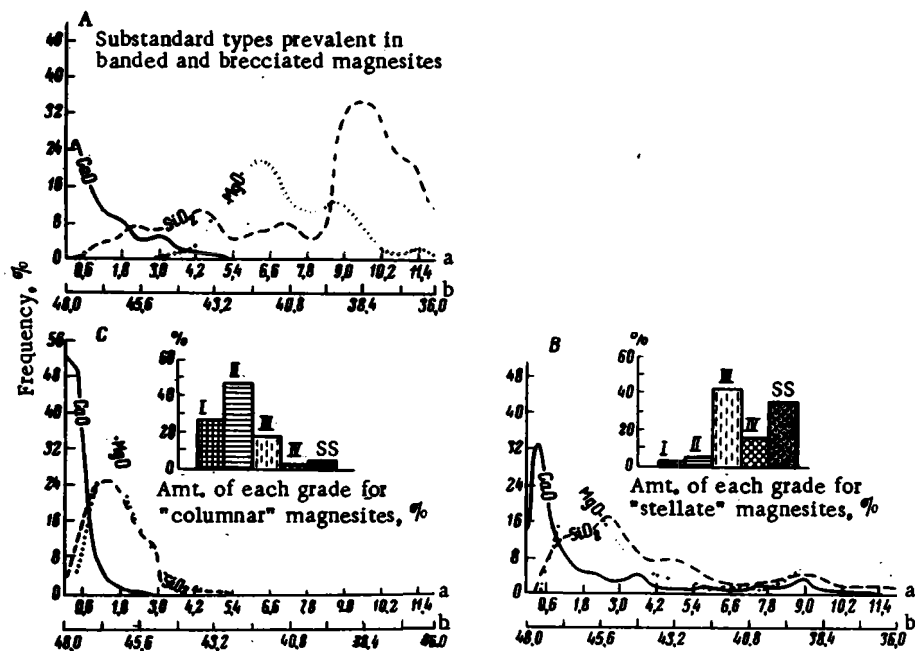


Fig. 5. Distribution curves of basic components in individual textural types of magnesite: a) for silica and calcium oxide; b) for magnesium oxide. Number of analyses by rock group: A, 1250; B, 2310; C, 1760.

QUALITY OF THE MAGNESITE ORES

The results of an analysis of 15,000 channel and core samples taken from the Savina magnesites indicate a considerable variation in the content of the main components that determine the commercial value of the resource (MgO , CaO , SiO_2 , R_2O_3 , ignition loss).

Study of monomineralic fractions of individual textural types of the ore shows that they are very similar in their content of magnesium oxide (47.1-47.4%), calcium oxide (0.14-0.22%), and sesquioxides (Fe_2O_3 , 0.20-1.35%; Al_2O_3 , 0.03-0.63%).

A change in the amount of silicon oxide in the monomineralic fractions from 1.06-1.2% in marbly fine- and medium-grained types to 0.24% in columnar was found, which is apparently related to errors in extracting the fractions from the fine-grained ores. Such variations in the content of the basic components have practically no effect on the quality of the magnesite ore, the grading of which is determined by industrial requirements, as presented in Table 1 (Blinnikov et al., 1967).

Consequently, variations in the quality of magnesite ore depend on the amount of extraneous mineral material described above, which is quite irregularly distributed in the different textural types. The magnesite types can be subdivided according to a basic qualitative index into three groups: A, B, and C (Table 2). The data presented in the table show that qualitative differences in content of the main components between the different groups are very sharply expressed. Magnesites of Group A are characterized by a high content of silica (average 10.18%), a lower content of magnesium oxide (average 40.74%), and are relegated to substandard classes. Magnesites of group B (fine-grained, marbly, and "stellate"), considering all of the grades and substandard types encountered here as a whole, according

TABLE 1. Industrial Classification of the Savina Magnesite Ore

Magnesite grade	Content of main components, %			Magnesite grade	Content of main components, %		
	no less than	no more than			no less than	no more than	
	MgO	CaO	SiO ₂		MgO	CaO	SiO ₂
I	46,0	0,8	1,2	III	43,5	2,5	2,5
II	45,0	1,5	1,5	IV	43,5	2,5	7,0

TABLE 2. Chemical Composition of the Types of Magnesite Ore

Magnesite group by chem. comp.	Textural type	Content of component, %, from channel and core samples (numerator, limits of variation; denominator, average)				
		MgO	CaO	SiO ₂	R ₂ O ₃	ignition loss
A	Banded medium-grained and brecciated (1876 analyses)	$\frac{36,12-45,24}{40,74}$	$\frac{0,28-3,40}{1,63}$	$\frac{6,10-25,77}{10,18}$	$\frac{1,61-10,15}{4,86}$	29,16—44,56
B	Fine-grained (108 analyses)	$\frac{35,18-47,51}{45,19}$	$\frac{0,32-8,10}{1,87}$	$\frac{0,28-10,10}{2,17}$	$\frac{0,83-12,54}{1,81}$	23,15—50,90
	Marbly, medium-grained (3060 analyses)	$\frac{36,48-47,59}{44,76}$	$\frac{0,41-9,10}{1,82}$	$\frac{0,71-11,41}{2,68}$	$\frac{1,10-11,10}{1,89}$	21,98—50,30
	"Stellate" (5100 analyses)	$\frac{38,76-47,46}{45,28}$	$\frac{0,01-6,60}{1,37}$	$\frac{0,58-10,68}{2,97}$	$\frac{0,96-9,14}{1,78}$	22,68—51,20
C	Columnar and rod-shaped (4810 analyses)	$\frac{43,81-47,59}{46,31}$	$\frac{0,0-2,65}{0,62}$	$\frac{0,12-5,42}{1,27}$	$\frac{1,10-2,14}{1,53}$	
	Very coarsely crystalline	$\frac{44,22-47,59}{46,20}$	$\frac{0,0-1,84}{0,54}$	$\frac{0,14-4,47}{1,31}$	$\frac{0,90-2,31}{1,41}$	

Note. Chemical analyses from the laboratories of the Sayan Expedition of the Irkutsk Geological Survey by T. D. Boshernitsan, N. S. Sablina, Yu. F. Fadeeva, G. A. Sidorova, L. B. Poletaeva, and others.

TABLE 3. Chemical Composition of the Monomineralic Fraction of the Textural Types of Magnesite

Textural type	Content of component, % (numerator, limits of variation; denominator, average)					
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	ignition loss
Banded medium-grained and brecciated	Monomineralic fraction not studied					
Fine-grained (38 analyses)	46,54—47,27 47,19	0,10—0,16 0,14	0,63—2,71 1,22	0,46—1,31 1,09	0,04—0,20 0,09	49,04—52,07
Marbly, medium-grained (56 analyses)	46,18—47,27 47,18	0,05—0,46 0,22	0,16—2,30 1,06	0,42—1,35 1,19	0,03—0,63 0,19	47,61—52,14
"Stellate" (84 analyses)	46,18—47,36 47,29	0,15—0,16 0,15	0,19—1,75 0,73	0,46—1,28 1,11	0,03—0,18 0,11	50,95—51,45
Columnar (83 analyses)	46,60—47,40 47,10	0,0—0,30 0,20	0,03—0,70 0,24	0,20—1,23 1,12	0,05—0,15 0,13	50,28—51,36
Very coarsely crystalline (36 analyses)	46,88—47,37 47,22	0,0—0,27 0,16	0,10—0,75 0,21	0,34—1,23 1,16	0,04—0,14 0,13	50,64—51,45

Note. Chemical analyses from the laboratories of the Sayan Expedition of the Irkutsk Geological Survey by T. D. Boshernitsan.

to its content of silica (2.17-2.97%) and other components can be referred in the industrial classification only to grades III and IV. Columnar and rod-shaped magnesite (group C) are mainly in grades I and II (Table 3).

Statistical analyses of 6320 chemical analyses of channel and core samples over the entire central part of the industrial reserves, which is the most thoroughly prospected part (Fig. 4), provide frequency curves of the main components and diagrams of the grade ratios which quite graphically show the relationship of ore quality to the individual textural types (Fig. 5).

The pattern disclosed is also borne out by comparison of the geologic and ore-quality maps and sections in the central part of the deposit (see Fig. 4), in which an almost complete coincidence of the boundaries of the fields of different textural types and the grade of the magnesite ore is noted. An exception to this rule is seen only in the zone of introduction into the magnesites of such elements as silicon, iron, aluminum, calcium, etc. (the zone of intensive linear faulting and exocontacts of basic rock bodies).

Thus, the quality of the magnesite ore of metasomatic origin in the Savina deposit depends on the following basic factors.

1. The chemical composition of the original dolomite of the Kamchadal suite, at the expense of which the magnesite formed.
2. The effect of post-ore tectonics and processes of contact-infiltration metasomatism, associated with the emplacement of basic intrusive bodies.
3. The difference in chemical composition of the different textural types of magnesite.

The establishment of patterns of spatial distribution of the commercial types of magnesite makes it possible to: a) conduct further useful exploration within the area of carbonate rocks of the Kamchadal suite; and b) direct prospective exploitation enterprises toward the recognition of different grades of magnesite and those changes in quality which can result from the working out of different textural types of magnesite ore.

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ROLE OF SORPTION PROCESSES IN INTERPHASE DISTRIBUTION OF COPPER IN NATURAL WATERS

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UDC 550.42;541.183.2

The effect of pH, adsorbent/adsorptive ratio, and presence of other ions and other factors on the sorption of copper by river water suspensions, ground-up rocks, and iron hydroxide was studied. On the basis of the information obtained, certain patterns of interphase copper distribution are explained for surface waters in Georgia. An hypothesis is presented for the sorption mechanism.

The most important barrier to the migration of trace elements is the sorption processes occurring in reservoirs. In the role of sorbent are clay minerals, metal hydroxides, organic mineral suspensions, etc. (Krauskopf, 1963; Lobchenko and Kaplin, 1968; Solomin and Goncharova, 1968; Sanchez and Lee, 1973; Orlova, 1976).

The amount of trace-element sorption in river-water suspensions (under other individual conditions) depends on the dispersion of the adsorbent, the ratio of adsorbent to adsorptive, the presence of extraneous ions, temperature, and so on (Krauskopf, 1963; Solomin and Goncharova, 1968; Solomin and Lobchenko, 1968; Nilsen, 1968; O'Connor and Kester, 1975; Starik, 1969). There is especially great significance in interphase trace-element distribution, to the pH value, with whose increase the sorption of cations by clay minerals and hydroxides increases (Krauskopf, 1963; Solomin and Goncharova, 1968; Starik, 1969; Sanchez and Lee, 1973; O'Connor and Kester, 1975; Orlova, 1976).

General patterns in the sorption of electrolytes on clay minerals and metal hydroxides have been studied quite well. However, in order to clarify and evaluate their role in trace-element distribution in natural waters, data are necessary which have been obtained under actual conditions approximating nature. The majority of works carried out in the area of trace-element sorption does not correspond to this request.

In model suspensions, we studied the effect of certain factors on the sorption of copper by suspended matter. The composition of the suspension and sorption conditions approximated natural ones in feasibility. Suspensions were used as sorbents which were primarily separated from waters of the Aragvi and Alazani rivers (Aragvi-estuary, Apr. 9, 1975; Alazani-Gavazi, May 22, 1975), as well as rocks ground-up and separated into grain-size fractions (shales, sandstone) and iron hydroxide. The chemical and mineralogical composition of the sorbents used is described in the work by N. S. Goliadze, G. D. Supatashvili, and G. A. Chikhradze (1975).

The technique of the experiment consisted of the following: a solid phase was added to 0.5 liters of distilled or piped water and stirred, the necessary medium was created, and a given amount of copper was introduced in the form of a sulfate. The mixture was shaken several times in a 24-h period and after equilibrium was established, the content of copper was determined in the solution using lead diethyldithiocarbamate. The sorption of copper on the vessel walls (polyethylene) was insignificant and as a result had practically no effect.

Based on sorption capacity, the suspensions prepared from the ground-up rock were inferior to the natural ones (suspensions separated from river waters). The amount of copper sorption in the natural suspensions was five to six times greater on the average than in the ground-up rocks. In other experiment series, it was established that a quantitative sorption of 110 μg of copper corresponded to 0.1-0.33 g/liter of suspension and more than 1 g/liter of ground-up rock. The differing sorption capacity is caused by the different mineralogical and grain-size compositions of the sorbents indicated. With an increase in

Tbilisi State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 99-104, November-December, 1977. Original article submitted April 5, 1977.

TABLE 1. Effect of the Adsorptive/Adsorbent Ratio on Copper Sorption

Initial copper concentrate, $\mu\text{g/liter}$	Adsorbent concentrate (suspensions), g/liter	$\text{Cu}_{\text{init}} \cdot 10^3$ suspensions	Equilibrium concentrate of copper, $\mu\text{g/liter}$	Cu sorbed	
				%	$\mu\text{moles/g}$
20	0,50	0,04	0,5	97,5	0,62
40	0,50	0,08	14	65	0,82
80	0,50	0,16	32	60	1,50
120	0,50	0,24	64	47	1,76
200	0,50	0,40	116	42	2,64
100	4,00	0,03	3	97	0,36
100	2,00	0,05	7	93	0,73
100	1,20	0,08	12	88	1,15
100	1,00	0,10	20	80	1,24
100	0,40	0,25	41	59	2,32
100	0,20	0,50	55	45	3,55
100	0,12	0,83	60	40	5,25
100	0,04	2,50	63	37	14,5

the dispersion of rocks from 0.3 to 0.01 mm in size, the amount of sorbed copper in a recalculation on the basis of 1 g of sorbent increases on the average from 200 to 270 μg . This may explain the increase in copper content in fine suspensions in the rivers of Georgia. Fractionation of the suspensions was done by settling of the natural waters. The finest suspension fractions are especially rich in copper, where the average copper content is 0.022%, which is 4.7 times greater than clark.

The ratio of absorptive concentrate to adsorbent turns out to have a great influence on the sorption of copper, and as a result of this, on its interphase distribution in basins. The significance of this factor is especially important for surface waters in Georgia, in which the suspension content varies within broad limits. We have previously found that an inverse association is observed between turbidity and copper content in suspensions in the rivers of Georgia.

In order to explain this fact in model suspensions, the effect of the adsorptive/adsorbent ratio on the amount of copper sorption was studied. Ground-up rocks, shales, and sandstone (0.02-0.03-mm fraction) were used as sorbents. The sorption capacities of the rocks used turned out to be similar; therefore, we were limited by the results obtained in the shale (Table 1). With an increase in adsorptive/adsorbent ratio, the equilibrium concentrate and amount of copper sorption ($\mu\text{moles/g}$) increased, and the completeness of sorp-

tion $\left(\frac{\text{Cu}_{\text{sorb}}}{\text{Cu}_{\text{init}}} 100\% \right)$ decreased. An especially sharp change in these values is observed in the

initial region of low adsorptive-adsorbent values ($\leq 10^{-4}$). The river waters of Georgia belong to just such systems. Assuming that Cu_{init} in river waters is more or less constant, copper concentrate in the suspensions should be in inverse relation to the content of the solid phase. This is actually observed. The reason for the inverse relation between the turbidity of river waters and copper content in the suspensions may also be the increase in size of the suspended particles with an increase in their overall content in the basins.

Extending the results obtained in the model suspensions to natural waters, considering the equilibrium concentrate of copper in them and its content in the solid phase, we deduce that the integral concentrate of copper in the river waters of Georgia are equal to $\approx 60 \mu\text{g/liter}$.

Metal hydroxides are good sorbents of trace elements in natural waters (Krauskopf, 1963; Solomin and Goncharova, 1968; Orlova, 1976). Under natural conditions, the presence of iron, manganese, and aluminum hydroxides is most probable (Vinogradov, 1967). The last is recommended for the concentrate of copper from natural waters (Supatashvili et al., 1974). Iron hydroxide is also an active sorbent (Table 2). Equilibrium is established, practically speaking, in the course of 1-3 h. Iron hydroxide preserves quite a good sorption capacity even after aging of the precipitate underwater (Fig. 1). Even the air-dried matter from the solution sorbs a significant amount of copper (see Table 2). The opinion is confirmed that in natural waters sorption on metal hydroxides prevails, and not coprecipitation of trace elements (Solomin and Goncharova, 1968).

Iron hydroxide noticeably exceeds the ground-up rocks and natural river suspensions in sorption capacity. At high $\text{Cu}_{\text{init}}/\text{Fe}(\text{OH})_3$ ratios (0.05-0.5), the amount of copper sorption

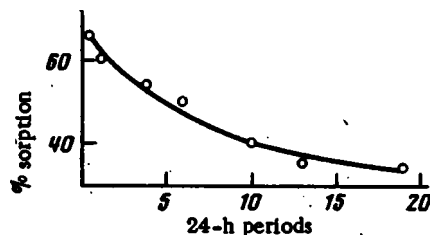


Fig. 1. Change in sorption capacity of iron hydroxide during aging (100 μg Cu^{++} , 10 mg $\text{Fe}(\text{OH})_3$, 500 ml water).

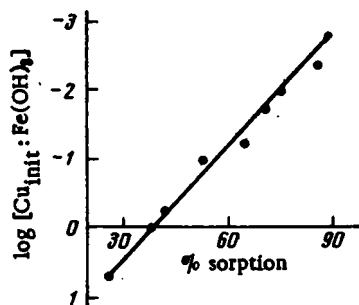


Fig. 2

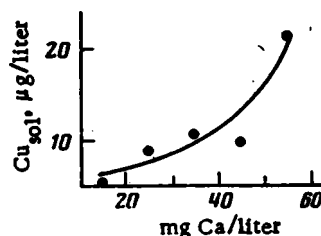


Fig. 3

Fig. 2. Copper sorption as a function of $\log [\text{Cu}_{\text{init}}:\text{Fe}(\text{OH})_3]$.

Fig. 3. Copper content as a function of calcium content in surface waters of Georgia (grouped data).

TABLE 2. Effect of Amount and Degree of Aging of Iron Hydroxide on Copper Sorption (50 μg of copper, pH 8.0 ± 0.1 , 0.5 liter twice-distilled water)

$\text{Fe}(\text{OH})_3$, mg	$\log \frac{\text{Cu}}{\text{Fe}(\text{OH})_3}$	Copper sorbed on $\text{Fe}(\text{OH})_3$, %		
		freshly precipitated	after 6 days' precipitation	air-dried
0.1	-0.30	28	5	2
0.5	-1.00	39	12	8
1.0	-1.30	45	20	15
5.0	-2.00	55	38	28
10	-2.30	65	52	40
30	-2.80	70	65	54
50	-3.00	74	71	60
100	-3.30	81	78	64
300	-3.80	95	88	74

is 0.36-2.05 μmoles for 1 g of wet, freshly precipitated sorbent. Thus, even small amounts of metal hydroxides may play an important role in the interphase distribution of copper in basins. The completeness of copper sorption, as in the cases considered above, is determined by the $\text{Cu}_{\text{init}}/\text{Fe}(\text{OH})_3$ ratio (Fig. 2).

The total sorption capacity of sediments in natural waters significantly exceeds the equilibrium concentrates of copper in the majority of cases. The question arises: What is the explanation for the presence of Cu_{init} in waters at an adequate suspension content? The answer must be sought in the complex composition of natural waters. Copper sorption on suspensions is subject to processes of complex-formation and the concurrence of other ions. We have previously shown (Supatashvili et al., 1974) that copper sorption on aluminum hydroxide in the presence of organic ligands is less, the greater their concentration and the greater the indicators of the instability constants (pK) of corresponding copper ions. The concurrence of other ions may play no small role. Based on the data of P. Nilsen (1968), noticeable concentrations of Fe^{++} and Mn^{++} are subordinate to copper sorption in feldspar grains.

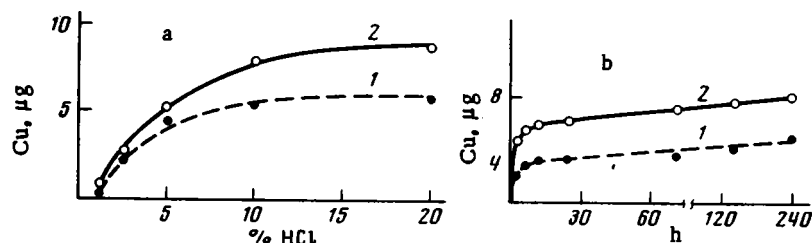


Fig. 4. Solubility of suspended copper as a function of HCl concentrate (a) and the duration of contact of the solid phase and the acid (b). 1) Bottom sediments, 2) suspensions (0.2 g of the solid phase, 50 ml HCl).

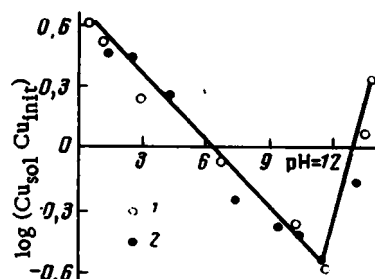


Fig. 5. Interphase distribution of copper as a function of pH. 1) Suspensions, 2) ground-up rocks (solid phase 0.25 g, 50 μg Cu^{++} , 500 ml of distilled water).

TABLE 3. Effect of Sodium and Calcium on Copper Sorption by Ground-Up Rocks (shales, sandstone 0.25 g, $d = 0.02-0.03$ mm, 50 μg of copper, 500 ml of twice-distilled water)

Na^+ , mg/liter	Copper sorption, %	Ca^{++} , mg/liter	Copper sorption, %
12	100	10	90
23	100	20	80
46	100	40	62
92	94	100	56
230	78	200	50
300	74	300	45
480	67	500	37
920	58	800	30

We studied the effect of the most important ions in natural waters upon copper sorption by suspensions. Into 0.5 liters of the bidistillate was introduced 0.25 g of suspensions separated from river waters, 50 μg of copper, and different amounts of sodium and calcium chlorides. After equilibrium was established in the liquid phase, copper content was determined. It was ascertained that the effect of a measured amount of sodium on copper sorption was insignificant (Table 3). At a content of 100 mg/liter of sodium, copper sorption was decreased by 10%. The effect of calcium was more noticeable: at a calcium concentration of 20 mg/liter, sorption decreased 20% and at twice the calcium concentration, 38%. Such a concentration of calcium is usual for surface waters.

Grouping data we obtained previously, a direct correlation is actually found between calcium and copper content in the surface waters of Georgia (Fig. 3). With an increase in calcium content in the basins, it is less distinct, but it is also possible to trace a decrease in copper content in the suspensions transported by the rivers. The presence of such an association is explained by the concurrent capacities of calcium ions and copper desorption with an increase in calcium concentration in the solution. Laboratory studies have

shown that 70% of the copper is desorbed from the suspensions with the introduction into the liquid phase of 1-2 mg/liter of calcium (in the form of chloride).

Study of the acid-soluble (mobile) forms of copper gives weighty information on the nature of sorption in suspensions and bottom deposits. The optimum concentration of HCl (10%) was selected empirically. The principal share of copper (70-80%) passes into the liquid phase in the course of 0.5-3 h, after which the process is slowed noticeably (Fig. 4). This provides an opportunity for suggesting that the "mobile" copper is concentrated on the surface of the solid phase or contained in the composition of the easily soluble substances (hydroxides, carbonates). Obtaining a unique answer to the internal volumetric distribution of copper in suspended matter is impossible without additional experimental information.

As a result of the acid activation of the clay minerals, due to the washing out of the soluble components and the formation of a new structure, the porosity of the sorbents is increased. With acid activation of the suspensions and bottom sediments in the Georgian basins (according to S. A. Orlova's procedure, 1976), copper sorption does not increase but decreases (on an average of 10%). Thus, in natural suspensions and bottom sediments, 98-99% of the copper is sorbed (0.2 g of the solid phase, 50 ml of twice-distilled water, 100 µg of copper). After acid activation under these conditions, 87-90% of the copper is sorbed. The decrease in sorption capacity of the suspensions after treatment with acids is explained by a solution of carbonates and hydroxides, which are good sorbents.

The coefficient of interphase distribution of copper clearly results in a change in the pH of the medium. With its increase to 11.5, copper sorption in the suspension increases linearly (Fig. 5), probably due to hydroxylation of the sorbent and the appearance of additional active centers (Orlova, 1976). With a further increase in the pH of the suspension, copper sorption decreases, which is probably due to the dominance of neutral and negatively charged hydroxyl complexes of copper.

The complicated, polymineralic composition of river-water suspensions makes it difficult to estimate the mechanism of copper sorption. The data presented in the literature (Lobchenko and Kaplin, 1968) as well as the results obtained by us indicate that ion-exchange processes are dominant in clay minerals. It is also impossible to deny the possibility of chemisorption processes occurring, since 10-20% of the copper sorbed into natural forms of suspensions and bottom sediments is not desorbed by 10% hydrochloric acid.

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COMPARATIVE STABILITY AND FORMATION CONDITIONS OF KAOLINITE AND HALLOYSITE

B. F. Gorbachev

UDC 549.623.91

Standard free energy values of halloysite formation have been calculated. Thermochemical levels were also calculated and stability diagrams constructed for kaolinite and halloysite. In contrast to kaolinite, halloysite is a metastable mineral that disintegrates in the zone of aeration. The length of geological time required for the total dissolution of metastable halloysite minerals and their replacement by more stable kaolinite was not considered in the present evaluation because the reaction speed, factors that control it, and the source of activation energy are unknown. An attempt was made at an exact definition of the physicochemical conditions of halloysite mineral stability and at the evaluation of the reliability of the results received by comparing them with geological and mineralogical research data.

Standard Free Energy of Halloysite Formation

Halloysite minerals in nature have the composition formula of



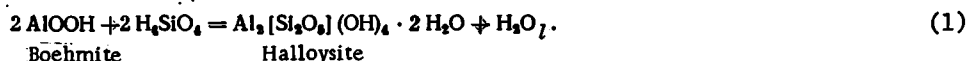
where $0 \leq n \leq 2$. The interlayer water content ranges between certain limits that allowed the distinction between hydrated ($n = 1.3-2.0$) and low-water-content ($n = 0.3-0.7$) halloysite varieties (Brindley and Goodyear, 1948). Only the most hydrated form ($n \approx 2$) with characteristic basal reflection at 10 Å is regarded as halloysite in the current domestic literature. Total removal of the interlayer waters irreversibly leads to the metahalloysite stage that has a basal reflection at 7.2 Å.

The evaluation of the relative stability of kaolinite and of the two halloysite forms at standard conditions (25°C and 1 atm pressure) is feasible by traditional thermochemical calculations which require no knowledge of the standard free energy of the mineral formation ($\Delta Z_{2,0}^\circ$). The $\Delta Z_{2,0}^\circ$ values, used in the calculations, are shown in Table 1.

It should be noted that an earlier value of $\Delta Z_{2,0}^\circ$ for halloysite (endellite), calculated as -902 ± 0.7 kcal/mole, from solubility data (Reesmann and Keller, 1968), apparently is too low. The authors disregarded the fact that during halloysite (endellite) dissolution the ionic equilibria are controlled by a stable phase of a newly formed substance. Kaolinite forms this substance the fastest. The danger of such an error in $\Delta Z_{2,0}^\circ$ determination on the basis of solubility has been recently demonstrated by I. K. Karpov and others (1974).

In order to obtain a more exact value of $\Delta Z_{2,0}^\circ$ for halloysite, we have employed two methods in calculating it.

1. The start was the reaction of halloysite synthesis when the dissolved silicic acid reacts with boehmite. It can be defined with the following chemical reaction:



The standard free energy of this reaction at 25°C can be calculated from the equal-temperature levels of the chemical reaction by the equation:

$$\Delta Z_{R1}^\circ = -RT \ln K = -1.364 \lg K = -1.364 \lg \frac{1}{[\text{H}_4\text{SiO}_4]^2} = 2.728 \lg [\text{H}_4\text{SiO}_4]. \quad (2)$$

All-Union Geological Scientific-Research Institute of Nonmetallic Minerals (VNIIGEOLNERUD), Kazan. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 105-113, November-December, 1977. Original article submitted January 12, 1976.

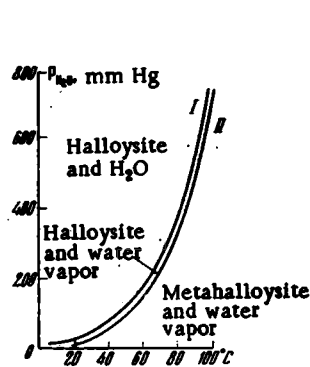


Fig. 1

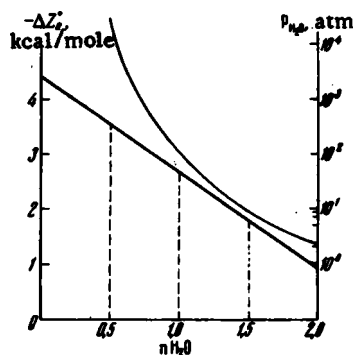


Fig. 2

Fig. 1. Halloysite dehydration curve (Sand and Bates, 1953): water vaporization curve (I); boundary curve between halloysite and metahalloysite (II).

Fig. 2. Function of the free energy values of the reaction (ΔZ°_R): halloysite→kaolinite transition as the function of the water-uptake (nH₂O) of the halloysite mineral. The water vapor-equilibrium pressure curve is also shown.

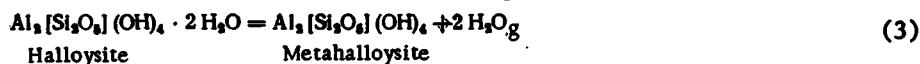
TABLE 1. Thermochemical Reference Data

Compounds, ions		ΔZ° ₂₉₈ , kcal/mole	Data source
Al ₂ [Si ₂ O ₅](OH) ₄	(Kaolinite)	903,0	Naumov et al. 1971
Al ₂ [Si ₂ O ₅](OH) ₄	(Metahalloysite)	898,55	Same 1971
H ₂ O _l	(Water)	56,687	> 1971
H ₂ O _g	(Water vapor)	54,634	> 1971
AlOOH	(Boehmite)	217,6	Reesman, Keller 1968
H ₂ SiO ₄	(Water solution)	312,8	Same 1965
Al ³⁺	(Same)	115,0	> 1969
Al(OH) ²⁺	>	164,9	> 1969
Al(OH) ₂ ⁺	>	261,1	> 1969
Al(OH) ₄ ⁻	>	311,1	> 1969

At pH values of <9, the solubility range of silicic acid in relatively amorphous silica is $10^{-2.6}$ – $10^{-2.7}$ mole/liter (Kittrick, 1969). By using this value in Eq. (2), the ΔZ°_R values obtained were -7.09 and -7.45 kcal/mole, respectively.

By using the calculated ΔZ°_R values, the standard free energy value (average) turns out to be -1011.38 kcal/mole. By an identical calculation we obtained the ΔZ°₂₉₈ value of metahalloysite (-898.01 kcal/mole), which is practically identical with an experimentally arrived value (-898.6 kcal/mole) of Robie and Waldbaum (1968). This proves the reliability of the calculation.

2. The dehydration reaction of halloysite is the following:



As the experimental data on halloysite dehydration (Fig. 1) shows, the balance between the two halloysitic minerals is accomplished at 25°C at a water vapor pressure of ~20 mm Hg (0.0255 atm). By inserting this value into Eq. (2), we find that

$$\begin{aligned} \Delta Z_{R_0}^{\circ} &= -1.363 [\text{H}_2\text{O}]^2 = -2.7281 \lg \text{H}_2\text{O} = -2.6728 \lg 10^{-1.59} = 4.35 \text{ kcal/mole,} \\ \Delta Z_{298}^{\circ} \text{Halloysite} &= \Delta Z_{298}^{\circ} \text{Metahalloysite} + 2\Delta Z^{\circ} \text{Water vapor} - \Delta Z_{R_0}^{\circ} = \\ &= -898.55 + (-2 \cdot 54.634) - 4.35 = -1012.17 \text{ kcal/mole.} \end{aligned}$$

Thus, the results received from two separate calculation methods are completely compatible. However, in the second calculation the equilibrium vapor pressure is an approximate value. Therefore, the first value of ΔZ°₂₉₈ for halloysite is more satisfactory (-1011.38 ± 1.5 kcal/mole).

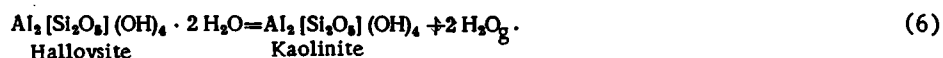
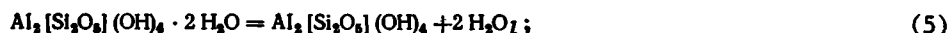
STABILITY DIAGRAMS

Stability comparison between kaolinite and metahalloysite under standard conditions has been made earlier by Huang (1974) by a thermochemical analysis of the reaction:



It has been demonstrated that the value of $\Delta Z^\circ_{R_4}$ is -4.5 kcal/mole (-4.45 , according to our calculations). The reaction may spontaneously proceed from left to right. This means that metahalloysite is a metastable phase and with time it will completely convert into kaolinite. The speed of metahalloysite dissolution and kaolinite formation is determined by the activation energy and temperature conditions. The quoted thermochemical calculations apply to a system where a complete halloysite dehydration takes place. However, we realize that halloysite in nature is in different stages of hydration.

The $\Delta Z^\circ_{2,8}$ values of halloysite offer a basis for comparing its stability with that of kaolinite. The following equations are used:



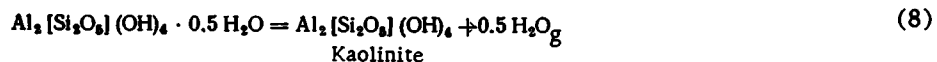
By employing the values of $\Delta Z^\circ_{2,8}$ for the initial and final products of the reactions in the calculations (Table 1), the standard free energy values of reactions (5) and (6) turned out to be -4.99 and -0.89 kcal/mole, respectively. Consequently, under standard conditions, these reactions may spontaneously move in the direction of kaolinite formation. Reaction (5) is more efficient than (6), from the energy viewpoint. In reaction (5), theoretically, equilibria occur only at higher temperatures. As the specific heat of halloysite is not yet established, the equilibrium temperature cannot be established.

In reaction (6), the equilibrium partial pressure of water vapor equals

$$\lg P_{\text{H}_2\text{O}} = \frac{0.89}{2.728} = 0.326; P_{\text{H}_2\text{O}} = 2.12 \text{ atm}. \quad (7)$$

Since at lower temperatures the water vapor pressure is unattainable, the most probable process is the replacement of halloysite by kaolinite.

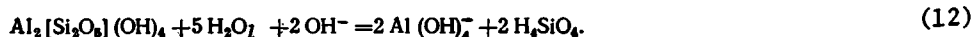
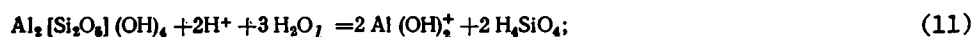
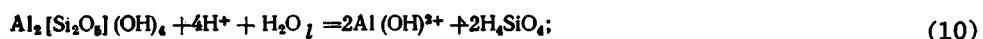
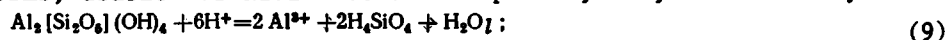
Under conditions of aeration, especially when the relative atmospheric humidity is less than 80%, halloysite dehydration is a much faster process. High water tables create mostly low-water halloysite varieties that are strongly metastable in comparison with kaolinite. Thus, in the reaction:



the calculated $\Delta Z^\circ_{2,8}$ value is -3.56 kcal/mole. The equilibrium vapor pressure at 25°C theoretically requires several thousand atm (Fig. 2) pressure, which does not occur on the earth's surface. In view of this, it can be assumed that reaction (8) occurs spontaneously and practically irreversibly in the zone of hypergenesis during kaolinite formation. Evidently, given sufficient geologic time, the reaction is completed.

In the reverse process, kaolinite replacement by halloysite is completed under hydrothermal conditions, when water vapor pressures exceed the equilibrium conditions at given temperatures. However, only halloysite proper and none of its low-water forms develop in this case.

A number of equations relating to chemical reactions of solution have been reviewed for the construction of stability diagrams. Huang and Keller (1973) published equations for the roles of various ionic Al-forms, usable for kaolinite and completely dehydrated halloysite:



Similar equations have been compiled for halloysite:

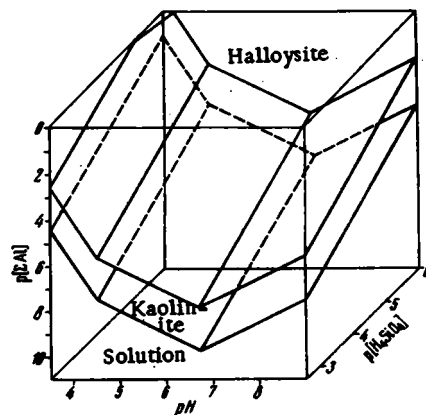
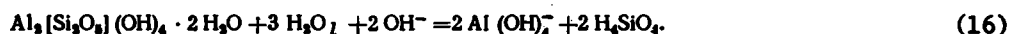
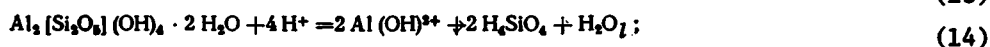
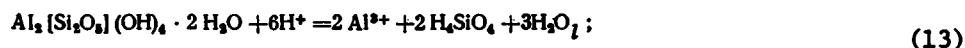


Fig. 3. Kaolinite and halloysite stability in solution, as the function of silicic acid and Al activity, and pH, at 25°C and 1 atm.

TABLE 2. Equations Relating to Equilibrium Conditions of the Kaolinite Group with Silicic Acid and Ionic Forms of Al Dissolved in Water Solutions

Left side of equation	Right side of equation	
	kaolinite	halloysite
$\lg[\text{Al}^{3+}] + \lg[\text{H}_4\text{SiO}_4]$	3.40—3 pH	5.23—3 pH
$\lg[\text{Al}(\text{OH})^{2+}] + \lg[\text{H}_4\text{SiO}_4]$	— 1.57—2 pH	0.26—2 pH
$\lg[\text{Al}(\text{OH})^{2+}] + \lg[\text{H}_2\text{SiO}_4]$	— 5.59— pH	—3.76— pH
$\lg[\text{Al}(\text{OH})^{4-}] + \lg[\text{H}_4\text{SiO}_4]$	—18.92+ pH	—17.08+ pH



Thermochemical equations (Table 2) were derived from the calculations of $\Delta Z_{R,-1}^0$ values after their substitution in formula $\Delta Z_R^0 = -1.364 \log K$.

Table 2 shows kaolinite more stable than halloysite, as its equilibrium with the solution occurs at much (by approximately two orders of magnitude) lower total activity of silicic acid and Al ions in the solution. When calculated (e.g., $10^{-2.6}$ and 10^{-6} mole/liter) silicic acid activity values are assigned to a solution, the Al ion equilibrium activity of the pH = 4–9 interval can be determined. A block diagram (Fig. 3) shows relative kaolinite and halloysite stabilities by using the $p[\text{Al}]$ — $p[\text{H}_2\text{SiO}_4]$ —pH coordinates. As the proportion of the dissolved silicic acid formed at pH = 9 never exceeds 20% (Huang and Keller, 1973), their impact on the total silica activity in the solution was not considered. In the light of our data, the assumptions on the effects various pH values have on kaolinite and halloysite formation are clearly unfounded.

Discussion of Results

Kaolinite and halloysite minerals are found either together or separately in weathering products and in hydrothermal products of argillitization. The factors that determine whether kaolinite or halloysite occurs as the primary product in a given instance can be determined from the stability diagram (Fig. 3); from ion concentration values in natural solution. When a solution becomes oversaturated with respect to halloysite, conditions become favorable for the formation of both halloysite and kaolinite. In solutions that are saturated with respect to kaolinite, but are not saturated with respect to halloysite, only

kaolinite may precipitate. This conclusion has originally been made in analyzing the interaction between kaolinite and metahalloysite (Huang, 1974). Huang's analysis is unsatisfactory since metahalloysite cannot be considered a primary phase.

Solutions in nature are commonly supersaturated with respect to halloysite; most frequently when: 1) alkaline or acidic solutions are neutralized; 2) the temperatures of mineralized waters are lowered; 3) dissolved gases are lost from the solutions.

When conditions in the media change sufficiently abruptly for the formation of colloid suspensions, aluminosilicate gels (allophane varieties) develop. According to a number of researchers (Rus'ko and Ivanov, 1970; Parham, 1969a, b), halloysite forms during feldspar weathering from earlier-developed aluminosilicate gels. At the same time, assumptions on a colloidal stage in the formation of eluvial kaolinite remained unsubstantiated (Rus'ko, 1972). The assumption on colloidal halloysite formation is in certain agreement with observations of globular halloysite microaggregates (Chukhrov, 1970; Sudo and Takahashi, 1956; Diamond and Bloor, 1970). Their morphology bears a close resemblance to metacolloidal substances. In addition, observations by Vernet (1970) on the interrelationships between globular and tubular halloysite precipitates in thin sections suggest that these crystallized directly from the oversaturated solution.

The factors that favor halloysite formation are the following: 1) the presence of such rock-forming minerals in the substrate source that are not very stable in the presence of water (plagioclase feldspars and feldspathoids); 2) a control provided by the composition and structure of acidic plagioclase feldspars (Chekin et al., 1972); 3) a low degree of order in the Si and Al atom arrangement in the volcanic glass source material (Keller, 1963); 4) oxidation processes of native sulfur and sulfides that produce most aggressive sulfuric acid.

All researchers agree that metahalloysite always forms through halloysite dehydration (Beits et al., 1962; Chukhrov et al., 1966; Brindley and Goodyear, 1948; Roy and Osborn, 1954). When halloysite is completely dehydrated in the zone of aeration, the interlayer distance between the 1:1 silicate layers is reduced from 5.7 to 3 Å (Beits et al., 1962). Later data (Churchman et al., 1972) suggest that dehydration during the intermediate stages results in alternating hydrated and dehydrated layers in the crystal structure, with a tendency toward their partial segregation.

Relationships typical of crystal hydrates exist between hydrated and dehydrated halloysite forms: 1) in contrast to loss of zeolite water, dehydration occurs with changes in the crystal structure; 2) a stable, linear relationship exists between values of $\Delta Z_{2,0}^0$ and the number of crystalline water molecules (Fig. 4).

Spontaneous halloysite dehydration accompanied by gradual decline in water vapor pressure occurs slowly and becomes important only when the relative atmospheric humidity is less than 30%. It stops when humidity declines below 20% (Brindley and Goodyear, 1948; Harrison and Greenberg, 1962). The stability of the relationship between interlayer water and the halloysite structure was shown by G. O. Piloyan and E. P. Val'yashikhina (1970). A similar conduct of halloysite during dehydration is in complete agreement with our calculations, based on the Kelvin formula, modified for slit-shaped capillaries (Greg and Sing, 1970). Interlayer water may exist at relative atmospheric humidities of not less than 16%. Since halloysite dehydration has a diffusional mechanism (Piloyan and Val'yashikhina, 1970), individual crystals incorporated into loose products of the weathering horizon will dehydrate fastest. In dense, monomineralic concentrates (fracture-filling concretions) halloysite accumulation may take much longer.

The problem of the genetic interrelationship between kaolinite and the two halloysite varieties has been insufficiently studied. While halloysite minerals and kaolinite are quite widespread in contemporary weathering products and soils, kaolinite predominates in the clay fractions of old weathering horizons. Assumptions on the metastable character of halloysitic substances, based on the analysis of their distribution in geological materials of differing ages and on thermochemical considerations, are further confirmed by a number of direct and indirect data. A few are listed in the following:

1. Electron-microscopy studies by Parham (1969a) led to the conclusion that during weathering and model experiments feldspars are primarily replaced by halloysite that later converts into kaolinite.

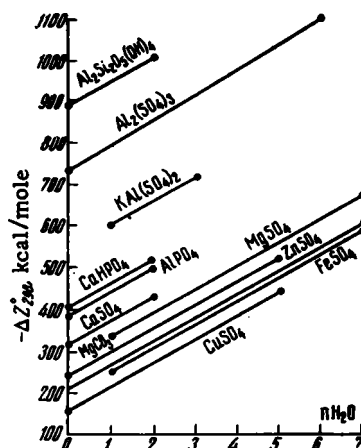


Fig. 4. Relationship between standard free energy ($-\Delta Z_{298}^{\circ}$) of halloysitic mineral formation and the number of inter-layer water molecules. For comparison, similar relationships are also shown between typical crystal hydrates and their dehydration products.

2. In comparison with kaolinite, halloysite is found in deeper (relatively younger) horizons of kaolinitic weathering horizons (Chekin et al., 1972).
3. Halloysitic minerals are absent in sedimentary clays (Vikulova, 1973). This shows that during sediment diagenesis supersaturation is insufficient to result in halloysite formation.

Structural studies revealed the typical two-layered structure of halloysite (Chukhrov et al., 1966). This presented an obstacle in the clarification of how metastable halloysite converts into stable kaolinite. Under natural conditions, the degradation of halloysite structure (dissolution) and the formation of the kaolinitic structure (crystallization) takes place. The process speed, its controlling factors, the sources of the needed activation energy, all require specialized studies. It follows from the previous thermochemical calculations that in the zone of complete water saturation the metastable character of halloysite, compared with kaolinite, is more apparent than in the zone of aeration. This does not deny the geological fact that halloysite (along with kaolinite) occurs mostly in deposits close to the surface (in weathering horizons and soils, resiliified bauxites, infiltration zones and in zones of low-temperature hydrothermal argillitization). The activation energy that sustains the halloysite-kaolinite reaction is derived from numerous geochemical processes within the zone of hypergenesis. The most common of these are the microbiological reactions and the radiolytic decomposition of water.

Based on the thermochemical calculations, it is expected that halloysite formation is accompanied by various morphogenic stages. Prismatic crystals, tubular forms, packets of layers with curled margins form and, in time, all may be replaced later by platy precipitates and their aggregates, typical of kaolinite. A partially similar process probably is often found in electron-microscope studies, but has not yet been sufficiently interpreted. The most interesting features include, e.g., hexagonal end-surfaces of halloysitic crystals, shown in several published photos (Beits and Komer, 1962; Gritsaenko et al., 1961).

CONCLUSIONS

Halloysite is a metastable mineral formed during feldspar weathering or through the effect of lower-temperature ascending waters on feldspars. The minerals precipitate from natural aluminum solutions that are supersaturated with respect to halloysite.

A more exact standard free energy value of halloysite formation has been calculated ($\Delta Z_{298}^{\circ} = -1011.38 \pm 1.5$ kcal/mole).

The behavior of halloysite during dehydration is similar to that of typical crystal hydrates. The speed and degree of spontaneous halloysite dehydration are determined by the water vapor pressure. The most dehydrated halloysite varieties occur at relative humidities of $\leq 16\%$.

The thermochemical calculations indicate that, given enough time, the halloysitic minerals may be completely replaced by the more stable kaolinite. This process probably is the most effective in the zone of complete water saturation.

The reaction speed, the factors that control it, and the sources of activation energy that fuel the process require further detailed studies.

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DETRITAL SEDIMENT ORIENTATION IN GROUND MORAINES OF THE NORTHERN
DVINA AND VYCHEGDA RIVER BASINS

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UDC 552.122:551.332.21(470.11)

The most typical feature of the bouldery argillaceous loams of the Northern Dvina and Vychegda river basins is their platy structure formed by laminar-plastic movement of ice that deposited the moraines. This character of the moraine outcrops is emphasized by filmy sand-silt coatings ("prisypki") and iron hydroxide precipitates at the contact between sediment units of different textures. These coatings relate to the redeposition of sand-silt particles on the surfaces of such units at the time when blue bands and streaks of regelated ice formed (Lavrushin, 1969, 1976).

The general appearance and character of the platy structure relates to laminar-plastic ice flow characteristics and, to some extent, to the grain-size composition of the incorporated material. Most often, the platy structure in the Dneprovsk and Moskovsk moraines is very clearly shown by plane-parallel sheets that had been expressions of the banded structure of ice that transported the moraine material (Lavrushin, 1969). Well-developed platy boudinage of a reticulated pattern reflects it most often. It is related to the termination in a given direction, of lenslike layers within the clean or the morainal ice (Evteev, 1965). The thickness of individual plate-bands in the moraines ranges between 5-15 cm.

This type of banded structure is much less common in the Kalininsk and Ostashkovsk moraines, possibly due to their higher clay content and to the redeposition of too many fine-grained particles on the unit interfaces. They cannot easily be distinguished granulometrically from the material that forms the plates. Platyness is so poorly developed here that it is almost completely hidden by the columnar parting, typical of the Kalininsk and Ostashkovsk moraines of the Northern Dvina River basin.

In a number of outcrops of these moraines (Fig. 1; Seftra Landing at Pustynya village; at Kopachevo village), however, the platyness is very clearly expressed. It bears a close resemblance to distinct lenses and layers of sand-loam morainal material along contact surfaces, present in the platy category. This platyness of the morainal deposits may be due to the uneven concentration of bedding surfaces that separate the plates, that formed of material, actively entrained by the accumulating glacier. In this case, moraines show well-developed banded structures, emphasized by the sandy makeup of the entrained material.

Argillaceous-coarse detrital moraines are widespread in the area with structural features, indicative of plastic flow. They are relatively thick and uniform in vertical sections and occupy large areas. They conform with the dynamic-platy morainal facies as defined by Lavrushin (1976).

Certain compositional features of the ground moraines are dependent on and controlled by the layered-plastic flow of the moraine-bearing ice. One such characteristic may be the long axis orientation of detrital grains parallel with the ice flow direction (Shantser, 1966, et al.).

Orientation studies of coarse detrital material in the ground moraines of the area are important in establishing a connection between them and the glaciation centers. A large research project on the subject has been undertaken in the Northern Dvina and Vychegda river basins by Field Party No. 14 of the All-Union Aerogeological Trust. The author has participated in this project between 1963-1971. The research confirmed that the Dneprovsk moraine in the Vychegda basin is related to the Novaya Zemlya-Ural glaciation center, while the Dneprovsk, Moskovsk, Kalininsk, and Ostashkovsk moraines of the Northern Dvina basin and the Moskovsk moraine of the Vychegda River basin are related to the Scandinavian Ice Sheet. This factor, due to the clearly established data, offers a unique stratigraphic characteris-

Moscow State University, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 114-118, November-December, 1977. Original article submitted June 21, 1976.

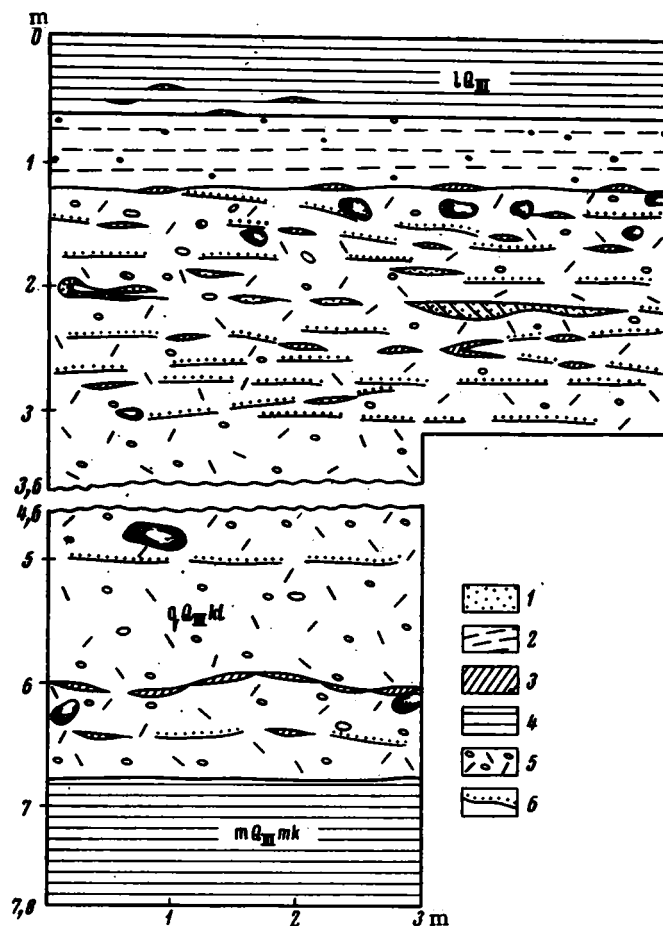


Fig. 1. Platy structure of the Kalininsk moraine in the Pustynya village outcrop by the Northern Dvina River. 1) Sand; 2) sandy loam; 3) loam; 4) clay; 5) loam with boulders; 6) contact plane between platy units.

tic, that — along with other information — allowed determination of the ground moraine's stratigraphic position (Nemtsova, 1975).

The orientation of the long pebble and boulder axes agrees well with their petrographic composition, and unequivocally identifies the positions of the glaciation centers. Detailed studies of the orientation of the coarse detrital material in the ground moraines indicated the quite complex configuration of glacier movements in the subject area. In particular, the lobe-shaped glacier outlines have been identified (Nemtsova, 1973).

In addition to the orientation of the coarse-detrital particles, for the first time in the Northern Dvina and Vychegda basins the author also conducted field studies on the orientation of elongated gravel particles. Concurrently, she also undertook microscopic studies on the orientation of elongated sand and silt particles found in the ground moraine.

Determination of the orientation of the gravelly and sand-silt material has great significance in the study of moraines that contain only small amounts of coarse material. Such moraines include the Kalininsk and Ostashkovsk moraines in the Northern Dvina basin. In addition, definition of the orientation of sand-silt particles in thin sections also allows the layer-by-layer analysis of the orientation of elongated particles. This is usually impossible in field work conducted on coarse moraine material.

In a number of key sections of moraines of different ages, the author has conducted parallel studies on both the coarse- and the fine-grained detrital material (Fig. 2). In most instances, the measurement results showed great similarities. Apparently, as sand-silt particles are much smaller than gravel, they react much more sensitively to changes in the direction and conditions of transport.

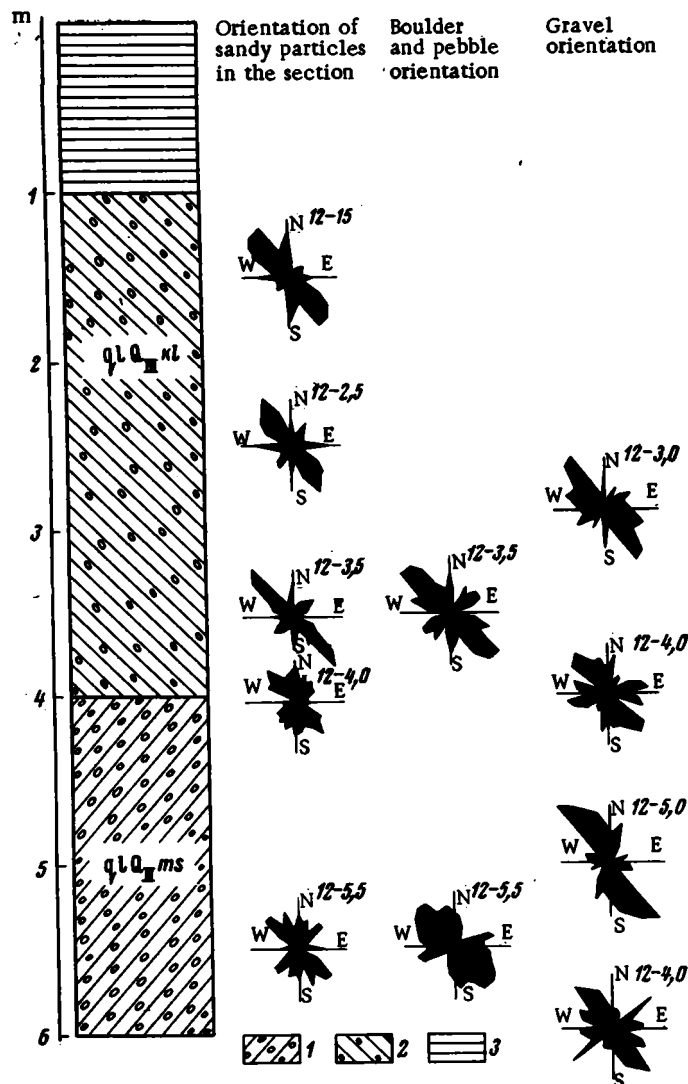


Fig. 2. Orientation of detrital material in the Moskovsk and Kalininsk moraines in section at Butyrskogo village on the Northern Dvina River. 1) Loam with boulder, Moskovsk periods; 2) loam with boulders, Kalininsk period; 3) clay.

The main maximum of small-particle orientation is shown in the diagrams. It clearly reflects the general direction of glacier movement, also identified in the study area by measured orientations of coarse-detrital particles and by striation directions on boulder pavements (Lavrov, 1970). However, in addition to the main orientation maximum of sand-silt particles, one or two transverse maxima were also observed at times. They are due to a number of causes, the most important of them being the often inclined positions of the particles' long axes. The horizontal sectional plane, shown in the oriented thin sections, created an apparent elongation of the grain sections in the transverse direction, absent longitudinally. Another reason for the transverse maxima is the masking of coarse particles by smaller ones.

The studied orientation rose diagrams of sand-silt particles of the Dneprovsk moraine by the villages of Slobodchikovo, Litvinovo, and Ryabovo also indicated certain trends of orientation maxima changes throughout the sections. The transport direction changed from the bottom toward the top of the sections, from a SSW to a SW direction. Field Party No. 14 of the All-Union Aerogeological Trust found the same in the orientation of coarse-detrital material in the Dneprovsk moraine section by Litvinovo. An explanation was offered for the phenomenon. The author suggests that the cause may be the weakened glacier activity toward the end of the glacial period when topography of the Vychegda valley might have taken over the control of the flow direction of the glacier that occupied the valley.

Orientation studies of detrital materials in ground moraines are important in their structural and textural analysis. The study of the textural characteristics of ground moraines is the primary and most responsive tool in identifying the origins of their composition.

The platy structure and the well-defined orientation of detrital particles of bouldery, argillaceous loams in the Northern Dvina and Vychegda basin moraines clearly indicate continental glaciers as the source of the moraines.

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TITANIUM MINERALS IN THE BOSHNYAKOVSK FORMATION ON SAKHALIN ISLAND

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UDC 553.494.2(571.64)

Authigenic Ti-minerals are widespread in sedimentary rocks and have been described by numerous authors (Kossovskaya, 1962, et al). They are generally considered to have formed from detrital leucoxene. N. V. Rengarten (1956) described anatase and brookite from sandstones in coal-bearing rocks in Karaganda. She thought that the minerals formed through the disintegration of plant matter.

Authigenic Ti-minerals are most common in deposits of the Upper Maastrichtian-Danian Boshnyak Formation of Sakhalin Island. The formation is composed of volcanosedimentary and terrigenous rocks and is subdivided into two units, a lower coal-bearing unit and an upper one, without coal. In certain areas, the upper unit contains near-shore-marine fossils. The granulometric composition is most varied and ranges from conglomerates to argillites. The sediments are in the late stage of early epigenesis. Coals of Unit "G" are included in the formation; with an abundance of heulandite, disordered, mixed-layer illitic-montmorillonitic minerals. Primary-detrital structures are typical in the rocks. The total thickness of the formation ranges between 500-700 m.

The authigenic Ti-minerals in these rocks are represented by leucoxene, anatase, and, rarely, sphene.

Leucoxene is found as detrital grains and authigenic substances in sandstone and siltstone cement where it surrounds rock fragments as a film (especially the basic and intermediate effusive rock fragments). It also occurs as isolated clusters in pores. Often it was partially recrystallized and transformed into finely crystalline anatase. In the argillites, the mineral is irregularly distributed and mixed with fine clayey matter. Spectrum analysis data show that the Ti content of the argillites is 0.5-0.6%.

Anatase is present in two varieties. The first is composed of irregular grains that are aggregates of minute crystal which are hard to identify. They have typical brownish-red and

Sakhalin Regional Geological Survey, Yuzhno-Sakhalinsk. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 118-120, November-December, 1977. Original article submitted December 20, 1976.

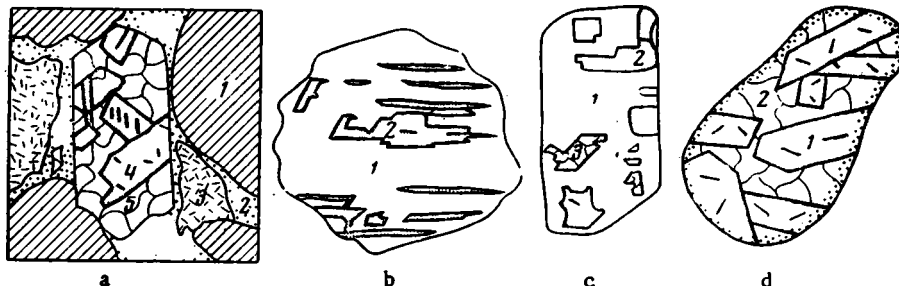


Fig. 1. Anatas formation from ilmenite. a) Anatas and quartz pseudomorphosis from tabular, angular ilmenite crystals: 1) ilmenite; 2) cryptocrystalline anatas; 3) chlorite; 4) crystalline anatas; 5) quartz; b, c) stages in ilmenite recrystallization: 1) ilmenite; 2) anatas; 3) quartz; d) quartz and anatas pseudomorphs from rounded ilmenite grains: 1) anatas; 2) quartz.

reddish-brown polarized hues. The second category is found in rocks as brown, elongated, prismatic crystals, with bipyramids and as tabular crystals with sizes of 0.008-0.02 mm.

The discussed anatas varieties often form unusual geodes. The partitions are composed of fine-grained anatas and the interior is filled by well-developed anatas and quartz crystals (Fig. 1d). Quartz sometimes is replaced by chlorite, rarely by chalcedony or kaolinite. Similar mineralizations sometimes are found in the pelitic fraction and form 1-2% of the rock. They have been found both in pyroclastic and in terrigenous rocks.

Formation of the discussed geodes can be best explained in the ilmenitic sandstones that underlie the Boshnyakovsk Formation at Snezhinka River. These sandstones underlie a sequence of interlayered sandstones, siltstones, and clay argillites. The upper part of the unit includes a 40-cm-thick coal bed. The ilmenite-bearing sandstone beds are 20 cm thick on the average.

The lower layer is the richest in ilmenite. Ilmenite grains, 0.1-0.2 mm in size, make up 95% of all fragments. They are well-rounded; rarely, poorly rounded — slightly rounded crystals also occur. All fragments are fringed by fine-grained anatas. The intergranular pore space is filled by green chlorite with radial-lamellated structure.

Large portions of the ilmenite grains disintegrated into various smaller-sized fragments. Some are only slightly corroded along the interface between anatas and quartz grains, others have been replaced to a significant extent by other minerals (Fig. 1b, c). When ilmenite is completely replaced, clearly defined, sometimes oriented, anatas and quartz crystals develop along the ilmenite cleavage planes. The shapes of the replaced ilmenite grains are completely preserved (Fig. 1a); if the rounded grains are completely replaced, no ilmenite characteristic is preserved. Such pseudomorphs take up the exact shapes of such voids. Their walls are encrusted by anatas and the voids filled by quartz.

Tufogenic sandstones of the upper layer are composed of ilmenite (50% of the fragments), feldspar fragments (25%), chloritized volcanic glass (20%), and strongly chloritized oligoclase (5%). The fragments are covered by a leucoxene film; the central parts of the pores filled by carbonate or by one of the previously mentioned minerals. Only 40% of the ilmenite grains are preserved in a relatively fresh state. The remaining 60% is composed of anatas and quartz pseudomorphs. Ilmenite disintegration is also accompanied by sagenite formation.

The upper ilmenite-bearing layer is represented by vitroclastic tuff, composed of volcanic glass fragments, with frequent flow structures. Ilmenite and its pseudomorphs occupy about 5% of the rock space. The dominant replacement affects ilmenite. It is accompanied by sagenite formation. The number of anatas-quartz pseudomorphs is sharply lower.

Study of the ilmenite-bearing sandstones revealed that ilmenite served as the basic source of authigenic Ti-minerals in rocks of the Boshnyak Formation. It shows a variety of replacement forms. Ilmenite disintegration with leucoxene and sagenite formation occurs by anatas and quartz replacement, without preliminary leucoxene development.

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ZEOLITES IN CRETACEOUS DEPOSITS OF THE KHATANGA BASIN
(NORTHEASTERN SIBERIA)

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UDC [542.674.3:551.763]+552.5(571.51)

Cretaceous deposits of the Khatanga Basin include terrigenous deposits of various facies, representing rhythmic interlayering of sands, silts, clays, with coal beds, fragments of carbonified and mineralized woody material, with carbonate concretions and silicate grains. The total sediment thickness is 1-1.7 km.

The zeolite mineralization is found in alluvial-lacustrine, coal-bearing, Upper Hauterivian-Aptian deposits (Tigvansk and lower Sangasalinsk Formations) in the Kotuy River (Battagai River) basin, and lagoonal-marine Turonian-Campanian deposits in the Kheta River basin. These sediments are 200, respectively, and 350 m thick.

The basic, detrital rock-forming components of the Cretaceous units are represented by quartz, various feldspars, and rock fragments. Siliceous rock fragments play an important role among the rock fragments. They are finely aggraded, with radiating structures ($n_{\text{mean}} = 1.512-1.530$). Although lesser in amount, but still important (forming 30-50% of all the rock fragments) are grains of basic effusives, chloritized and carbonatized to various degrees. The admixtures include fragments of clayey, siliceous-clayey, sericitic-clayey rocks of microquartzites and acidic effusives. According to immersion data by T. V. Ukhina, N. G. Berzhets, Z. N. Ipatova, and L. G. Kubasova, the heavy fraction of the rocks is dominated by ilmenite (maximum 90%). Occasionally, high epidote (maximum 30%) and hornblende concentrations (maximum 40%) also occur. Magnetite, Fe-hydroxide, leucoxene, Ti-minerals of uncertain identity, anatase, sphene, zircon, garnets (mostly of the pyrop-almandine-spessartine group) make up 5-10% (maximum 20%) of the heavy fraction. Minor admixtures include rutile, tourmaline, orthite, staurolite, spinel, disthene, chloritoid, monazite, xenotime, amphiboles of the actinolite-tremolite group, brookite and hypersthene. The clayey fraction of the silt-sand and clayey rocks is mostly of smectitic and illite-chlorite-smectite composition. Unusual "glaucinitelike" silicate grains are also found in continental-lagoonal deposits, that contain smectite and chlorite-bearing sediments. In the marine deposits they contain smectite and illite.

On the basis of the detrital components three rock types can be identified: siliceous rocks, basic arkoses, and porphyritic-siliceous graywackes (Fig. 1). In the first group, quartz is typically abundant and K-varieties are common among the feldspars. In the heavy fraction, ilmenite predominates. The second group has high concentrations of basic oligoclase and andesine feldspars with labradorite grains and certain amounts of sphene, amphiboles, sometimes epidote in the heavy fraction. The porphyritic-siliceous graywackes, confined to the Ledianaya Formation, are essentially terrigenous-chemical rocks, basically with smectite-chlorite composition. Genetically, they are both synthetic and formed from fragments of basic effusives. They are also mixed with the cement that often contains aragonitic carbonates. The detrital rock fraction is rich in basic effusive rock fragments, and especially in silica material; the heavy fraction almost completely is composed of ilmenite.

The rock composition was determined by the mixing of material, derived from the Taimyr folded zone and the northern part of the Siberian Platform. The sediments were locally differentiated and affected by extensive weathering. The Taimyr source area is characterized

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Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 120-124, November-December, 1977. Original article submitted June 15, 1976.

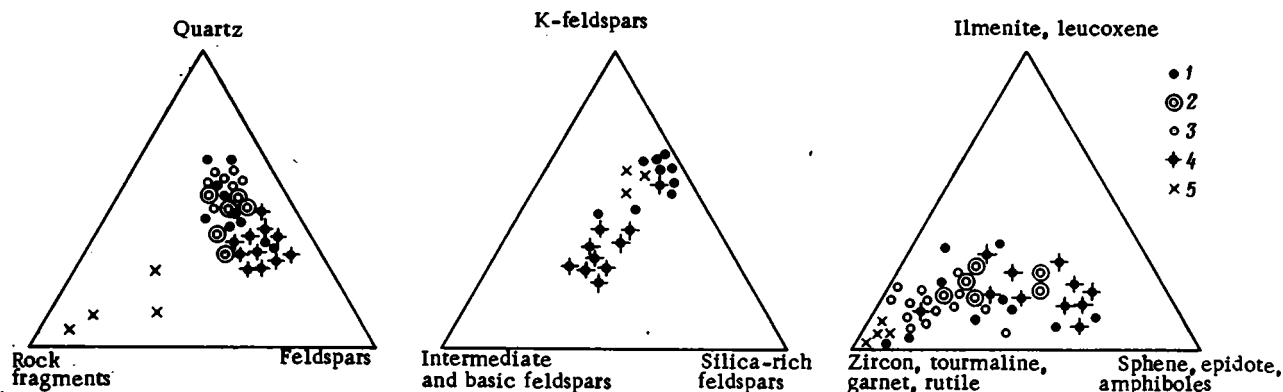


Fig. 1. Composition of silt-sand Cretaceous rocks (0.01-0.1-mm size fraction) in the Kotuy River basin (Lower Cretaceous Tigysansk and Sangasalinsk Formations) and the Kheta River basin (Upper Cretaceous Ledyanaya and Khetsk Formation and Santonian-Campanian units). Deposits: 1) Lower Cretaceous, coal-bearing; 2) coal-bearing; 3) lagoonal-marine; zeolites; 4) mostly plagioclase-derived; 5) synthetic and terrigenous-chemical deposits.

TABLE 1. Chemical Analyses of Zeolites

Sam- ple No.	Section, age	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	TiO ₂	P ₂ O ₅	MnO	CaO	MgO	K ₂ O	Na ₂ O	CaCh. loss	Total
8a	Ledyanaya R., Ledyanaya Fonn.	57,77	15,47	2,69	—	0,17	—	0,05	4,48	2,39	1,38	0,62	15,42	100,44
2a*	Battagai R., Tig- yansk Fonn.	60,61	18,92	1,68	0,73	0,42	0,13	0,05	3,00	0,31	3,25	2,03	7,91	99,64

*Includes significant admixtures of quartz and feldspars. Analysis by V. M. Tumina.

by ilmenite and epidote that are typical of the greenschist formation of the Gornyi Taimyr area (Ronkina, 1965; Korobova, 1973). Monazite and xenotime are known from the cataclastic granitoids of the area (Ravich and Chaika, 1962). These are metamorphic minerals.

The abundance of the Taimyr ilmenite and epidote, that replace magnetite and clinozoisite from Platform sources, is typical of the pre-Upper Hauterivian deposits (Ronkina, 1965), and indicates the rejuvenation of the land relief in the Taimyr folded belt during the Cretaceous.

The trap basalts of the Siberian Platform and crystalline schists of the Anabar Massif are the sources of smectitic clay deposits, fragments of basic effusives and siliceous formations (that formed during disintegration of chalcedony in the amygdulose of the trap rocks). Intermediate plagioclase feldspars, sphene, hornblende are also present. Rutile, tourmaline, zircon, spinel, and garnets were found in all rock types in uniform, low concentrations. They were located mostly in older sedimentary rocks. Differentiation resulted in concentrations of fine-grained, siliceous and stable sediments from the distant Taimyr source area and in abundant, unstable Ca-minerals in the coarser, particularly continental coal-bearing deposits, derived from the Siberian Platform. The weathering effect is manifested in the generally more acid character of the detrital components of the Upper Cretaceous deposits (Fig. 1), independently of their granulometric composition and facies features. The compositions of terrigenous-chemical rocks of the Ledyanaya Formation (abundance of stable components, ilmenite, silica, K-feldspars), and possibly, the uniformly high concentration of the authigenic mineralizations during the Late Cretaceous also reflect the effects of weathering.

Z. Z. Ronkina (1965) first proved the presence of zeolites in the lagoonal-marine Upper Cretaceous Ledyanaya Formation. Zeolites are present in all sections in that formation. They were also found in a few samples of marine Upper Santonian-Campanian units but were absent from the coal-bearing Khetsk Formation that separates them. The zeolite content in the thin sections ranged between 1-20%, being 10% on the average. The value increased in the light fraction of certain samples to 60%. Odd-shaped zeolite crystals, maximum 0.3 mm in size, are found in the pore-space of the rocks and within the cell tissues of plant fragments.

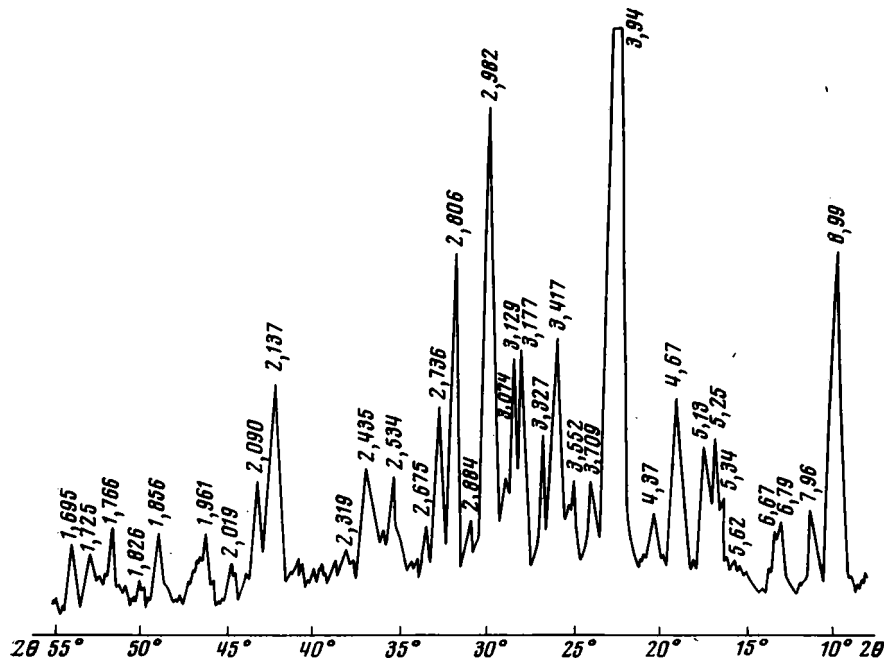


Fig. 2. Diffractogram of zeolite from the Ledyanaya Formation of the Kheta River basin (Ledyanaya River). Instrumentation: DRON-1; $\text{CuK}\alpha$ radiation.

The chemical (Table 1) and optical data ($n_g = 1.497$, $n_p = 1.486$, $+2V = 65-70^\circ$, negative elongation) shows that the zeolites are close to the heulandite form. The increased Fe_2O_3 and MgO content is due to admixtures of poorly crystallized, Mg-Fe bearing, Al-layer-silicates that make up the bulk of the zeolite-bearing rocks. The x-ray data (Fig. 2) indicate that the zeolites belong to the heulandite group. The zeolite diffractogram is closer to that of clinoptilolite than to heulandite (Boles, 1972).

In the Late Cretaceous coal-bearing deposits zeolites are less common. Zeolite content does not exceed a few percents and only rarely reaches 15-20% in the light fractions of certain samples. The refraction indices ($n_g = 1.496$; $n_p = 1.488$) of these zeolites are practically identical with those found in Upper Cretaceous deposits. It proved impossible to separate a pure zeolite fraction; the zeolite concentration was too low and they were thoroughly intermingled with feldspars. The chemical analysis of a fraction strongly contaminated by quartz, K-feldspars, and acid plagioclase feldspars (Table 1), indicates a rather calcitic zeolite composition. The basal reflections on the diffractogram (8.9, 3.95, 3.43, 2.97, 2.79 Å) are typical for the heulandite group and the intensity differences (less than 1.5-2 times) are insignificant.

In addition to the cited zeolites, a few isotropic zeolite grains ($n = 1.488-1.492$) have also been found in the light fraction of certain samples of Lower Cretaceous coal-bearing units, and primarily in Upper Cretaceous lagoonal-marine deposits.

The Cretaceous deposits of the Khatanga Basin thus exhibit two trends of zeolitization. In the first, few zeolite grains in the Lower Cretaceous coal-bearing units formed mostly from unstable Ca-plagioclase feldspars, derived from platform sources.

In the second trend, abundant zeolite mineralization developed synthetically in Upper Cretaceous lagoonal deposits, with numerous authigenic silicate grains. Stable minerals dominate the detrital association and no trace of pyroclastic material has been found in these rocks. Therefore, formation of zeolites and layer-silicates in this trend probably was favored by dissolved chemical products in partly closed, lagoonal sedimentary basins. These products were derived from weathering products of numerous trap areas in the Siberian Platform.

In both trends, the Ca-zeolites of the heulandite group are relatively poor in silica. This zeolite composition, in conjunction with the abundance of unique "granular" silicates and aragonite, and in the absence of authigenic silicate minerals, indicates relatively low

SiO₂ and high Ca-activity, related to the composition of unstable source materials (Ca-plagioclase feldspars). The presence of dissolved weathered products, derived from basic effusive rocks, and the hydrocarbonate-calcitic composition of the pore waters are typical of lagoonal-continental humid conditions.

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ORIGIN OF IRREGULAR SHAPES OF STAUROLITE GRAINS IN SEDIMENTARY ROCKS OF NORTH TIMAN

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UDC 549.611.21:552.51(234.83)

The so-called sawteeth on the ends of staurolite crystals in sedimentary rocks are well known. They are usually considered to be the result of either partial solution or authigenic growth within the sedimentary rock. Data confirming one or another point of view are unknown to the author. On the basis of personal observations on staurolite from Givetian rocks of North Timan, and on analysis of a great deal of literature, Preobrazhenskii (1941) concluded that staurolite (as well as other metamorphic minerals) may have grown during lithogenesis. This view was later confirmed by data from Timan and the Urals (Serd-yuchenko and Dobrotvorskaya, 1949) and disputed as basically incorrect (Sobolev et al., 1951). Some previously unnoticed features of staurolite from Givetian rocks of North Timan, which reveal the essential process of formation of such shapes at the ends of staurolite crystals, are presented below.

The writer has confirmed the data of Kochetkov (1967) on the presence of two types of staurolite within the Paleozoic clastic sequence, which differ in pleochroism and in the nature of their inclusions.

1. Staurolite, brown on Ng and brownish-yellow on Np, with abundant inclusions of quartz.
2. Staurolite, brown on Ng and greenish-yellow on Np. Quartz inclusions are sparse or absent.

It was established by study of thin sections and concentrates of staurolitic conglomerates that all of the crystals and grains of staurolite are replaced to some degree by a white aggregate. It was established optically to contain quartz ($n_e = 1.553$, $n_o = 1.544$) and a white platy mineral of the kaolinite group ($n_m = 1.566$). The accuracy of the identifications was confirmed by x-ray data. On careful crushing of the rocks, staurolite crystals are found within the concentrate, of which, when viewed from the ends, about 10-50% or more are composed of quartz and kaolinite, such that the original crystal form is relatively well preserved (Fig. 1). Complete pseudomorphs of staurolite are also found, composed entirely of these minerals. Observations of the nature of the distribution of the quartz inclusions in the original crystal, preserved in the core of the pseudomorphs and as quartz-kaolinite masses in the outer part, and also of incomplete pseudomorphs of crystals of the first and second kinds, suggests that the quartz is entirely from primary inclusions in staurolite.

Yurasskaya Expedition ATGU, Arkhangel. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 124-127, November-December, 1977. Original article submitted May 11, 1976.

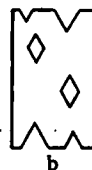
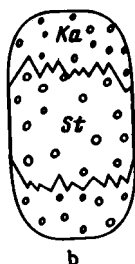
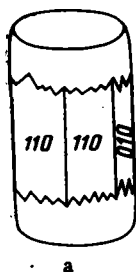


Fig. 1

Fig. 2

Fig. 1. Incomplete pseudomorphs of kaolinite after staurolite: a) general view; b) section. $\times 16$ (diagram from photograph).

Fig. 2. Schematic rendition of the original of sawtooth projections on the ends of staurolite crystals. Projections on the plane (110).

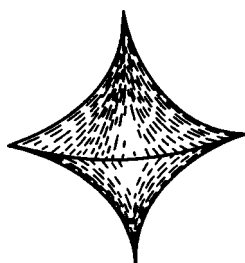


Fig. 3. Final form of solution of staurolite. $\times 20$.

On careful removal of the quartz-kaolinite material, "sawtooth" projections are revealed on the ends of the crystals which are similar to those which are cited in the literature as indicators of authigenic growth of staurolite in sedimentary rock. Thus, on the prism faces {110}, regular rhombohedral pits are always found (Fig. 2) which indicates that their "opening" on the edge of the third pinacoid is due to their position close to the ends of the crystal. The development of such open pyramids also leads to the appearance of distinctive "sawtooth" projections on the ends of the crystals. In the final stages, the sides of the pits are rounded by solution and curved surfaces are formed like those known in the crystals of other minerals (Shafranovskii, 1951). Maximum development of such surfaces leads to the appearance of the final form of solution (Fig. 3).

The two kinds of crystals mentioned form outwardly different final solution forms. In the first case, because of an abundance of quartz inclusions which bring about a high incidence of structural defects, a great many elementary pits of pyramids of solution are engendered and developed simultaneously. Merging together, they form an irregular "moth-eaten" body. On staurolite crystals containing no inclusions, few pits are etched to begin with, and subsequently no new ones are formed, but the original ones are deepened and widened as negative pyramids. As a result, the final form of the solution of the body is a doubly conical surface with staurolite symmetry. Observation of the final form of solution of both types of staurolite easily establishes that they differ only in the size and number of individual conical surfaces contained by the final form. The clearly formed large final solution form of the type shown in Fig. 3 is rarely encountered. More often crystals are developed with traces of solution, sawteeth forms, with varying degrees of development on the ends of the crystals.

Staurolite that is partially replaced by kaolinite is found only in the so-called staurolite horizon, which occurs in North Timan in the upper part of the middle Devonian Nadezhdin suite, a sequence of sandstones and conglomerates 50-285 m thick. It is overlain by three (locally more) sheets of basalt interbedded with beds and lenses of sandstone,

which are recognized as the late Devonian Kumushkin suite. The presence in places of pyritic galena- and barite-bearing cement with sphalerite and chalcopyrite, the origin of which is not entirely clear, is a feature of the middle Devonian conglomerates.

Geological conditions leading to this process should be associated either with the working over of staurolite-bearing sand and gravel during the post-volcanic phase of the basaltic flows by thermal waters which brought up from the depths various materials in solution, including a large amount of barium (Chernov, 1947), or with weathering processes on Precambrian garnet- and staurolite-bearing metamorphic rocks. The latter assumes the possibility of the transportation of incomplete pseudomorphs into the Givetian basin of sedimentation. Observation of such pseudomorphs in modern drainage basins indicates that they do not withstand transportation over a distance of a few kilometers. It is not excluded that similar conversions can occur as a result of the flushing of the sand-gravel sequence by meteoric water during weathering on land. In order to determine once and for all the place and conditions of this process, further work to this end is necessary. The writer wishes to emphasize herein only that the sawtooth projections on the ends of staurolite crystals from the Givetian deposits of Timan occurred as a result of reaction of solutions, and not growth, as believed earlier, and that kaolinite in the Devonian deposits (sandstones and conglomerates), if only partly, occurs at the expense of staurolite; and also to direct attention of investigators to the necessity of more thorough study of the complex shapes of crystals of mineral fragments in sedimentary rocks, especially if they are used as arguments for mode of origin.

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MIXED-LAYER MINERALS IN THE SERIES KAOLINITE-MONTMORILLONITE
IN THE OIL FIELDS OF NORTHERN SIBERIA

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and V. S. Kharin

UDC 549.623.91(571.1)

Mixed-layer kaolinite-montmorillonite minerals (MKMM) have been described in recent years by a number of investigators (Drits and Sakharov, 1974; D'yakonov and Kulikova, 1975; Sakharov and Drits, 1975; Chernyakovskii et al., 1975). The results of these studies have confirmed our conclusions as to the presence of MKMM in petroleum-bearing deposits of West Siberia (Metodika..., 1970; Ushatinskii and Babitsyn, 1970).

The minerals studied were rather widely distributed in Mesozoic-Cenozoic deposits of the sedimentary mantle of the West Siberian Platform. These deposits are unfaulted and unmetamorphosed, and bedding is nearly horizontal. The MKMM are found most commonly in Upper Cretaceous sand-silt-clay sediments of near-shore-marine and subcontinental origin at depths of about 900-1300 m (Table 1). Their identifications were made by means of electronography (on an EVR-1) and x-ray structure analysis (DRON-1) using the methodology of Zvyagin (1964), Drits and Sakharov (1974), and Sakharov and Drits (1975).

The diagnostic features that distinguish MKMM from mechanically mixed kaolinite and montmorillonite on the electronogram are the absence of the split reflection (060) on the fifth ellipse of the electronogram, which indicates the occurrence of an average of their "unit cell" (pseudocell) in the magnitude of the parameter b . Moreover, these minerals are often characterized by low structural perfection. An electronogram of mixed-layer kaolinite-montmorillonite is presented in Fig. 1a (sample 29a, Tazov area, hole 6r, depth of 1242-1245 m). As can be seen from the picture, kaolinite and montmorillonite reflections are present on the electronogram. The reflections (060) are not split. The "unit cell" (pseudocell) parameters are: $a = 5.17$, $b = 8.96$ Å. Kaolinite with these cell dimensions is not found in the rocks studied (Metodika..., 1970). The "unit cell" of kaolinite is pseudomonoclinical, and the structure is imperfect (disordered), which is apparent from the geometric pattern of the reflections on the electronogram. The reflection $k \neq 3k'$ is a solid ellipse, so that there is no periodicity on the c axis. The reflection $k = 3k'$ is not grouped in fours. The reflection $20\bar{L} + 1$ has a high intensity. The middle reflections $13\bar{L}$ and $13\bar{L} + 1$ are blurred and cannot be distinguished from one another, and run together with the edge of the reflection $20\bar{L}$. The border of the blurred, diffused band of merged reflections is barely distinguishable. The reflections $k \neq 3k'$ for montmorillonite also form a solid ellipse and completely coincide with those of kaolinite. The reflections $k = 3k'$ for montmorillonite are barely distinguishable and mainly blend with those of kaolinite. According to data from the electron microscope (Fig. 1b and c), particles of the samples studied are characterized by specific morphological features. Their outlines are indistinct, and they sometimes have a poorly expressed pseudo-hexagonal, or more often rounded, shape. It is impossible to call such particles either kaolinite or montmorillonite.

The work of Drits and Sakharov (1974) and Sakharov and Drits (1975) suggests that in the case of two-component mixed-layer structures with kaolinite and montmorillonite, reflections with an interplanar spacing of $d = 3.56-3.57$ Å are always present on the diffractogram, essentially without regard to the ratio of different types of layers. Just such a case is seen in sample 63 from the Urengoi gas field (hole 9, depth of 1185-1191 m) (Fig. 2a and b). In a saturated ethylene glycol preparation, reflections with $d = 7.87$, 7.90 , 8.22 , 8.43 and 3.57 Å appear on the diffraction diagram. According to the graphic value of d as a function of the content of montmorillonite layers (W_m) in structurally disordered minerals (Drits and Sakharov, 1974; Sakharov and Drits, 1975), the ratio of kaolinitic (W_k) to montmorillonitic (W_m) layers would here be 0.77:0.23, 0.70:0.30, 0.62:0.38, and 0.52:0.48. In

North-Siberian Scientific-Research Geological Petroleum Exploration Institute, Tyumen.
Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 127-131, November-December, 1977. Original article submitted August 4, 1976.

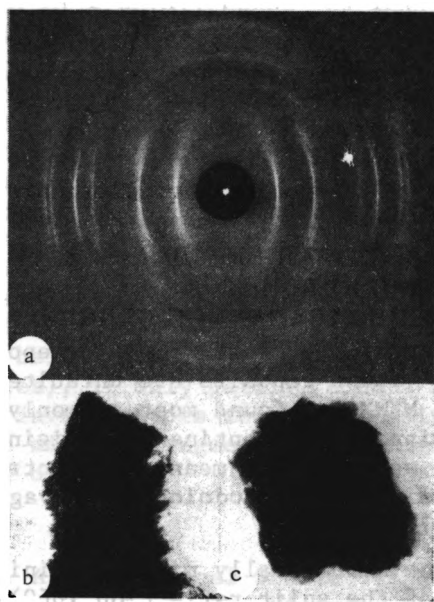


Fig. 1

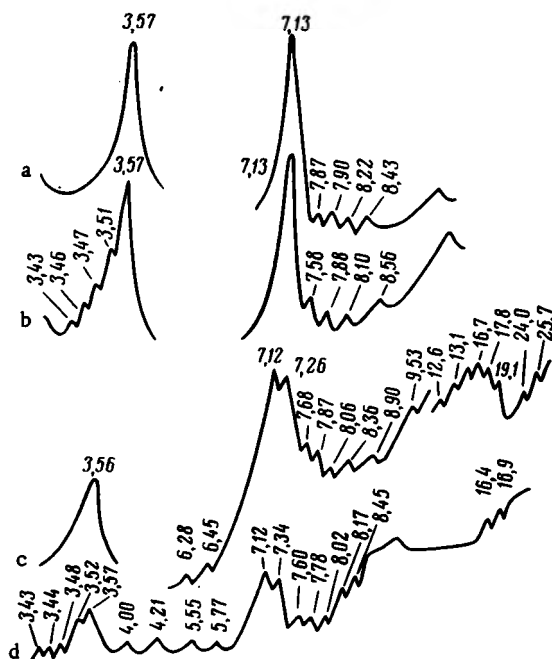


Fig. 2

Fig. 1. Electronogram (a) and electron-microscope photos (b, c, $\times 15,000$) of mixed-layer kaolinite-montmorillonite minerals. Sample 29a.

Fig. 2. Diffractogram of mixed-layer kaolinite-montmorillonite minerals: a, c) preparation, saturated ethylene glycol; b, d) dehydrated by heating to 350°C ; a, b) sample 63; c, d) sample 29a.

TABLE 1. Mineral Composition of Clayey Material in Samples from the Urengoi and Tazov Areas

Sample No.	Hole No.	Depth, m	Rock	Mineral composition
Urengoi area				
4	5r	715,1	Clay	K; MM; H; KM; C
3	2r	913,7	"	M; K; H; MM; KM; C
5	2r	952,7	Siltstone	M; K; MM; H; KM; C
10a	9r	1131,2	Sandstone	K; M; KM; H; MM; C
63	9r	1188,3	"	K; MM; H; KM
24a	6	1210,67	Siltstone	K; M; H; KM;
114a	9r	1252	Clay	M; K; H; KM; C
1	1r	1940,3	"	K; H; MM; KM; C
10	1r	2192	Sandstone	K; H; MM; KM; C
Tazov area				
7a	3r	1052,5	Clay	MM; K; C; KM
17a	3r	1070,4	"	M; H; K; C; MM; KM
43a	3r	1093,2	"	M; K; H; MM; C; KM
56a	3r	1105,8	"	M; K; H; MM; C; KM
76a	3r	1123	"	K; H; MM; C; KM
33a	13r	1202,7	"	M; K; H; MM; C; KM
23a	6r	1230,6	"	M; K; H; MM; C; KM
29a	6r	1244,5	"	M; K; H; MM; C; KM

K, kaolinite; M, montmorillonite; H, hydromica; C, chlorite; MM, mixed-layer mineral of the hydromica-montmorillonite series; KM, mixed-layer mineral of the kaolinite-montmorillonite series.

a dehydrated preparation (thickness of the montmorillonite layer 9.9 Å), reflections with $d = 7.58$ and 3.51 ; 7.88 and 3.47 ; 8.1 and 3.46 ; 8.56 and 3.43 Å appear on the diffractogram, which correspond to $W_k:W_m = 0.79:0.21$; $0.70:0.30$; $0.62:0.38$; $0.52:0.48$. Thus, in both cases $W_k:W_m = 0.79-0.52:0.21-0.48$.

Thus, it was possible to distinguish with x rays four types of MKMM growths with different ratios of kaolinite to montmorillonite layers. Despite the relatively close values of W_m , and consequently also the ratio $W_k:W_m$, the results obtained are quite comparable and agree with the calculations (Drits and Sakharov, 1974; Sakharov and Drits, 1975).

The above-mentioned sample 29a is a more complex case. A diffractogram of the fraction less than 0.01 mm in size of this sample (see Fig. 2c and d) in saturated ethylene glycol and dehydrated preparations indicates the presence of various structural (nature of the alternating layers) types (growths) of MKMM (disordered, ordered, and with a tendency of segregations of various types of layers).

Disordered Structure. Reflections with $d = 7.26$, 7.68 , 7.87 , 8.06 , and 3.56 Å are seen on the diffractogram in a saturated ethylene glycol preparation (Fig. 2c). According to the graph of the value of d vs the content of montmorillonite layers W_m (Drits and Sakharov, 1974), the ratio $W_k:W_m$ would be $0.87:0.13$, $0.77:0.23$, $0.69:0.31$, $0.68:0.32$, i.e., $0.87-0.68:0.13-0.32$. In the dehydrated state (Fig. 2d), reflections appear on the diffractogram with $d = 7.34$ and 3.52 ; 7.60 and 3.48 ; 7.78 and 3.44 ; 8.02 and 3.43 Å, which correspond to $W_k:W_m = 0.97:0.13$; $0.77:0.23$; $0.70:0.30$; $0.68:0.32$; i.e., $W_k:W_m = 0.87-0.68:0.13-0.32$. The results agree quite closely. As in the previous case, we are again concerned with four segments of a disordered structure.

In the diffractogram of the sample in the saturated ethylene glycol preparation (Fig. 2c) the reflections $d = 6.28$, 6.45 Å and 12.6 , 13.1 Å are also recorded. Moreover, reflections are seen in the range of $d = 24-26$ Å (24 , 25.7 Å). This suggests that ordered structure is present in the sample in addition to disordered. According to the graph of d as a function of P_{mm} (Drits and Sakharov, 1974), there are ratios of $W_k:W_m = 0.5:0.5$ and $0.65:0.35$ at $P_{mm} \leq 0.2$. In the diffractogram with the dehydrated preparation (Fig. 2d) reflections with $d = 4.00$ and 4.21 Å, 5.55 and 5.77 Å, 8.17 and 8.45 Å, 16.38 and 16.9 Å appear, which also correspond to $W_k:W_m \cong 0.5:0.5$ and $0.65:0.35$. There are thus two segments of ordered structure in the study sample: $W_m = 0.5$ and 0.35 .

In addition to this, kaolinite and montmorillonite are found here in a segregated (free) state. On a diffractogram of a saturated ethylene glycol preparation, the reflections for $d = 7.12$ Å and for 16.68 ; 17.8 ; 19.09 Å and 8.36 ; 8.9 ; 9.53 Å are present, which corresponds to "pure" kaolinite and montmorillonite in three varieties that are distinguished (Metodika..., 1970) by their content of aluminum in octahedral and tetrahedral coordination (down to beidellite), and by the ratio of cations absorbed in interplanar intervals to the size of the charge of the layer.

Thus, the presence of MKMM in the study deposits has been definitely established by means of electronography as well as by the results of x-ray structure analysis. The electronographic data in this case make it possible to determine the total content of kaolinite layers in the samples examined, while the x-ray information provides their ratio and the nature of their alternation in each of the structural types (aggregates) individually.

We suggest that the origin of the MKMM in the deposits studied is as follows. In most cases these minerals are found in the pore spaces of sandstones, siltstones, and silty clays in association with kaolinite, montmorillonite (sometimes beidellite), and mixed-layer hydromica-montmorillonite minerals. Beds of finely dispersed marine clay overlying the late Cretaceous sandstone-siltstone sequence and clayey interbeds within the unit are composed mainly of montmorillonite. This is here, as in the sandy-silty rocks, an allogenic mineral, while the kaolinite present in the cement of sandstones is predominantly authigenic (Metodika..., 1970). This kaolinite is developed by alteration of feldspar in an acidic environment that is brought about in porous rocks by katagenesis of organic material. Under these conditions montmorillonite transition through a beidellitelike phase to kaolinite takes place. Mixed-layer kaolinite-montmorillonite is also an intermediate product of this transition.

Experimental data on the transformation of kaolinite to montmorillonite (Frank-Kamenetskii et al., 1975), as well as information on the origin of MKMM in the weathering zone and in other natural situations (D'yakanov and Kulikova, 1975; Chernyakhovskii et al., 1975) are not incompatible with our model.

It must be noted that MKMM are metastable compounds. In the rocks studied, which are rich in organic matter, they are rapidly altered to kaolinite. This is also confirmed by experimental data: in samples exposed to the air for 10 years these minerals are completely replaced by kaolinite, while they are preserved in samples kept in paraffin. The mechanism of this transition calls for special study. In most respects it will probably be similar to the experimentally established mechanism for the kaolinite-montmorillonite transformation (Frank-Kamenetskii et al., 1975).

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AREAL AND VERTICAL DISTRIBUTION OF CLAY MINERALS AND ZEOLITES IN THE MANGANESE SEAM IN THE EASTERN PART OF THE NIKOPOL DEPOSIT

N. A. Panchenko

Clay minerals and zeolites in the ore-bearing seam of the Nikopol Manganese deposit have not as yet been sufficiently studied (Nikopol Manganese Basin..., 1964; Kostyleva, 1957, 1961), so there is at present no consensus as to their composition or their areal or vertical distribution in the seam. Meanwhile, clay minerals with their ready adaptability to thermodynamic conditions are most important indicators that characterize the various steps and stages in post-sedimentation processes.

The writer has conducted detailed mineralogical studies by optical, x-ray, thermal, and chemical methods in the eastern part of the Nikopol deposit, in the Grushev-Basan area, and has obtained new information. Diffractograms were obtained by L. A. Zhluktenko in the Dnepropetrovsk Institute of Mineral Resources, using the URS-50I; DTA curves by N. N. Elakhovskaya in the Scientific-Research Institute of Geology, Dnepropetrovsk State University, on an FPK-55; and chemical analyses by P. I. Davidenko in the "Gikyuzhroda" central laboratories in Krivoi Rog.

The ore bed in the study area is vertically heterogeneous, and it has been divided into four members, each of which, as a rule, occurs throughout the area and is characterized by definitive features (Panchenko and Popov, 1972), so that the country rock samples selected can be accurately related to the vertical section. Samples for testing were taken from all of the active mines and quarries (Fig. 1).

Manganese Ore-Dressing Group, Marganets. Translated from *Litologiya i Poleznye Iskopayemye*, No. 6, pp. 131-134, November-December, 1977. Original article submitted November 10, 1975.

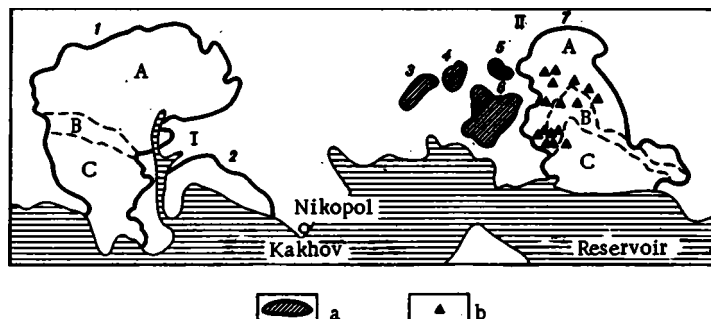


Fig. 1. Index map of the manganese ore districts in the Nikopol basin: I) Western ore district; areas: 1) main western deposit, 2) Sluts. II) Eastern ore district; areas: 3) Maksim-Timoshev, 4) Zakamen and Novoselov, 5) Nikolaev, 6) Komintern-Mar'ev, 7) Grushev-Basan. A) Manganese oxide ore; B) manganese oxide-carbonate ore; C) manganese carbonate ore. a) Worked out areas; b) country rock sample selection localities.

The country rock in the lower part of the ore bed (first member) is light-gray quartzose (in the zone of oxide ore) or quartzose-glauconitic sand (in the oxide-carbonate and carbonate ores). The main clay mineral is glauconite. In the oxide-ore zone, its content increases down dip from the edge of the deposit from scattered grains to a few percent, and in the oxide-carbonate and carbonate ore, up to 10-20 and locally 40%. Manganese-iron glauconite is found only in this part of the ore bed (Kostyleva, 1961); elsewhere it was not distinguished from iron-bearing varieties.

The country rock of the second member is macroscopically almost no different from the overlying members, but is less sticky. Locally greenish lenses 3-4 cm long are seen within the main light-gray mass. This difference is quite conspicuous under the microscope. A microlaminated texture with a very regular distribution of quartz grains is easily seen with crossed nichols.

Diffractionograms of this rock show a marked predominance of zeolite, and it has been determined by the principal interplanar spacings [sample 16, 8.9 Å (I = 8); 7.8 Å (I = 3); 5.06 Å (I = 4); 3.934 Å (I = 10)] to be clinoptillolite.

The wide development of clinoptillolite (as much as 15-20% of the entire rock) in the Paleogene Kiev and Kharkov deposits in the Nikopol region was pointed out by Butuzova (1964 a, b), who described the interrelationship of zeolites with other minerals. According to Kostyleva (1957) another zeolite, mordenite, is widespread in the country rock of the ore bed, but our investigation did not confirm this. Quartz and hydromica are found as accessory minerals (up to 3-10%) in the zeolitic country rock of the second member, and in lesser amounts, montmorillonite, glauconite, and nontronite.

The country rocks of the upper members have various hues and shades, but diffractiongrams and thermograms of their clays have shown that they have the same mineral composition, an aggregate of discrete grains of montmorillonite, hydromica, and accessory chlorite or kaolinite. A quantitative estimation of the content of individual clay minerals was made for these clays, according to the areas under the diffraction peaks as was outlined by Biscaye (1964). The accuracy of this method does not, in the writer's opinion, exceed 5-10%. According to the data obtained, the main clay minerals are montmorillonite and hydromica (Table 1).

Quartz, a common accessory (up to 20%) in the clays of the upper member, is distributed irregularly through the rock, sometimes close to the edge of the ore body. It forms lenses up to 40 cm thick of medium-grained sand. Glauconite is commonly found as individual grains or aggregates, and less commonly calcite, distributed throughout the country rock or at the boundary of the oxide and oxide-carbonate ores as patches that cement the country rock and ore nodules. Also found in places as cementing material in the oxide-carbonate zone are opal and chalcedony, and less commonly kaolinite-group minerals, chlorite, and zeolite.

TABLE 1. Clay Mineral Content in Country Rocks of the Manganese Bed

Sample No.	Content, %			
	mont-morillonite	hydromica	kaolinite	chlorite
127	73	27	—	—
128	47	53	—	—
129	60	32	—	8
139a	73	12	15	—
139b	49	47	4	—
148	45	55	—	—

As a rule, the members of the ore bed are separated from each other by interbeds 5-15 cm thick, lenses, and aggregates of pisolitic clay. The thickest and most widespread are the interbeds between the first and second, and especially between the second and third members. The picolites, which measure about 1 cm (rarely up to 5 cm), have a concentrically banded structure. Interbeds of this clay are of various shades (bluish-green, green, or yellowish-green, depending on degree of oxidation) and show up sharply against the background of the ore bed. The picolitic clay content in the ore bed is not large, generally up to 1%, but it is present everywhere throughout the deposit. It has been determined that 30-40% of the pisolites have massive, dense, dark brown nuclei 0.4-0.6 cm in diameter. Their composition was determined by x-ray powder pattern to be hydrogoethite (basic interplanar spacing, sample 137: 2.71 Å (I = 6); 2.44 Å (I = 10); 2.27 Å (I = 4); 1.71 Å (I = 8)) which was confirmed by a DTA curve with an endothermic effect around 315°C, characteristic for hydrogoethite (Ivanova et al., 1974).

The composition of the outer layers of the pisolites was determined by diffractogram as nontronite (basic interplanar spacing, sample 33a: 15.8 Å (I = 10); 4.48 Å (I = 10); 2.564 Å (I = 6); 1.509 Å (I = 7)). The first endothermic effect for this sample on the DTA curve at about 140°C was very strong, with an area many times greater than that of succeeding thermal effects, which is highly characteristic of nontronite (Ivanova et al., 1974). The chemical composition of the outer shells, wt %: SiO₂, 48.54; Al₂O₃, 0.92; Fe₂O₃, 29.42; FeO, 0.54; MnO, 1.74; CaO, 2.40; MgO, 3.50; Na₂O + K₂O, 0.50; SO₃, 0.44; P₂O₅, 0.09; ignition loss, 11.58. According to the content of iron and other main components the composition of the outer shells is closer to nontronite than to other clay minerals. Our studies confirmed the suggestion of Gryaznov et al. (Nikopol Manganese Ore Basin..., 1964), in their studies of pisolites without nuclei, that their composition was nontronitic. In the zone of oxide-carbonate ore the interbeds of pisolitic clay are commonly cemented by opal and chalcedony.

Thus, the investigations undertaken have shown that 1) there is a certain basic aluminosilicate mineral characteristic for each of the members of the ore bed: for the first, glauconite; for the second, clinoptillolite; for the third and fourth, hydromica and montmorillonite. Each member is separated from the others by interbeds, lenses, and aggregates of pisolitic clay of nontronitic composition; and that 2) the mineral composition of the aluminosilicates in the ore bed is determined by the ratio of member thickness and their content of the main aluminosilicate minerals. In the Grushev-Basan area, as in the entire Nikopol deposit, the thickness of the lower (glauconitic) member is generally considerably less than the other ones, so the mineral composition of the clay of the ore bed as a whole may be considered zeolitic-hydromicaceous-montmorillonitic.

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KAOLINITE PARTINGS IN COAL OF THE DONETS BASIN

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UDC 552.57:553.612(571.51)

A study of kaolinite partings in the Donets Basin, carried out by the writer over the course of more than 10 years, has had the objective of resolving disagreements over many problems on their conditions of formation, form and source of the original material, and agents of transportation, and also to explore the possibility of using them for stratigraphic subdivision and correlation of coal-bearing sections and synonymy of coal beds.

Previous studies on the composition of these partings in some of the coal seams of the basin (Bazilevich, 1941; Goretskii, 1941) were directed toward determining the possibility of using them as raw material for the refractory industry.

At the time of the Sixth Congress on the Stratigraphy and Geology of the Carboniferous (Great Britain, 1967) the writer had discovered and described tonsteins in 13 coal seams, mainly of middle Carboniferous age (Zaritskii, 1967, 1971a, 1971b). At present he has gathered information on the distribution within the basin, conditions of occurrence, and features of kaolinite partings, and also has carried out, in various degrees of detail, complex laboratory studies of this type of parting from 25 coal seams from all parts of the Carboniferous in various areas of the basin: c_1 , c_6^1 , c_8^n , c_{10}^v , c_{11} , g_2 , h_2 , h_4 , h_7 , h_{11} , i_3 , k_2^2 , k_3^v , k_5^1 , k_5^2 , k_6 , k_7^1 , k_8^n , l_1 , l_3 , l_8^1 , m_3 , m_5 , n_1 , and n_1^1 .

The kaolinite partings are easily recognized in the coal seam and differentiated from other coal partings by their compactness, sharp, tight contacts, light color (gray to dark gray) with brownish shades, rough fracture, and low hardness (scratched by fingernail). They are widely distributed and often are nearly as widespread as the coal bed containing them. For example, the kaolinite parting in the coal bed l_3 is developed over an area of several thousand square kilometers, or more than 200 km from west to east across the basin. This feature is an important geological indicator of the formation of peat bogs that do not lie in narrow bands along rivers but are laterally quite extensive. The position of the parting within the coal seam is fixed (for most seams it is in the upper part, for c_{11} and h_{11} in the middle, and for g_2 , k_6 , k_8^n and l_1 , in the lower part).

Mineralogical and petrographical studies (Zaritskii, 1967, 1970, 1973a) have established the development in the Donets Basin of all of the basic groups and types of tonsteins known in foreign basins. Granular tonsteins are represented by crystalline, coarse-grained, and pseudomorphic types. The most widely developed crystalline tonsteins are composed of coarse (tenths of millimeters, sometimes up to 1-2 mm) crystals of kaolinite, elongated along the c axis ("vermicules," "coin stacks," etc.), oriented along the bedding. Kaolinite crystals are sometimes found in a cryptocrystalline to finely crystalline kaolinitic groundmass. The ratio between the crystals and groundmass varies over a wide range, which make it possible to recognize a number of subtypes. Coarse-grained kaolinite partings found in individual coal seams are composed of opaline aggregates, grains of cryptocrystalline colorless kaolinite separated by a cryptocrystalline groundmass, enriched in carbonaceous matter, that is brownish in transmitted light. The pseudomorphic type of tonstein has been described so far only in the seam g_2 in the southern part of the basin. It is composed of kaolinitized grains of feldspar and mica, fine worm-shaped crystals of kaolinite, sharp fragments of quartz and a groundmass that reacts weakly to polarized light. Dense kaolinite partings are composed of a homogeneous kaolinite mass that is brownish in transmitted light

Kharkov State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 134-139, November-December, 1977. Original article submitted January 6, 1977.

and almost isotropic or weakly reacting (aggregately) in polarized light. The structural, textural, and mineralogical homogeneity of the rock is broken up by the presence of considerable amounts of carbonaceous grains of quartz and flakes of poorly hydrated mica of silt size. A subtype has also been described that is transitional between the dense and coarse-grained.

Detailed chemical and mineralogical studies, using chemical, thermal, x-ray, infrared spectroscopy, and crystal optic analyses, have established the kaolinitic composition of the coal partings. An exception is a montmorillonite parting in seam g_2 , which is developed over the area of the Petrikov deposit in the western Donets Basin (Brailovskaya, 1973). The silica modulus is generally close to or a little higher than the value for pure kaolinite (1.18), which is due to the presence of clastic quartz. In partings in the seams c_8^n , l_3 , and l_8^1 , on the other hand, the silica modulus is lower than the standard value, and direct determination established the presence of free aluminum up to 2-3%. The titanium modulus of the tonsteins is also close to the values for kaolinite in the weathering zone of the Ukrainian crystalline complex (0.025), but generally somewhat lower, and it varies among different beds over a rather wide range (0.006-0.026). Kaolinite partings from the coal seams c_8^1 , l_8^1 , and m_3 are distinguished among the tonsteins of the basin as having the lowest values of this index (0.006, 0.009, and 0.007, respectively). Bulk chemical analysis shows that the kaolinite partings are characterized by a constant composition with respect to their main components (including Al_2O_3 , TiO_2 , P_2O_5 , and others) over quite considerable areas.

Noting the remarkable lateral persistence of the basic character and composition of certain tonsteins, some essential distinctive features of partings within the same coal bed in hard coal and anthracite districts should also be pointed out. This is first of all concerned with alkaline and bound water. In anthracite regions the amount of alkaline water in partings is markedly higher, up to 6-8% (and bound water correspondingly lower), while in hard coal areas the alkaline water is found to be at low levels (tenths of a percent) and variable within a narrow range. In other words, if in the western and northern parts of the basin where coals are in the lower and middle stages of metamorphism these partings in different structural and petrographic situations are composed of kaolinite, then in areas with coals of the types T, PA, and A the rock-forming minerals are hydromica and muscovite (sometimes paragonite or paragonite-muscovite) (Zaritskii, 1967, 1970, 1973a). The size and shape of the vermiform and prismatic crystals remain practically the same, which suggests that the alteration of kaolinite to hydromica be ascribed to the post-diagenetic period.

Besides regional causes of the patterns of lateral alteration in the composition of tonsteins, a similar result can be achieved by the action of local factors: contact metamorphism, an example of which has been described by the writer in the Lower Silesian (Poland) coal basin (Zaritskii, 1972, 1973b).

As is known, the International Committee on Coal Petrography Nomenclature, taking into consideration the ambiguity of the term "tonstein," recommended that this type of coal parting be termed "kaolin-kohlentonstein" (International Dictionary, 1965). In connection with the fact that partings of this type are considerably altered locally or over a wide area by the effect of the factors mentioned above, they cannot be designated in this case by a term which includes the work "kaolinite". Although the writer has referred to the terms "tonstein" and "kaolin-kohlentonstein" critically (Zaritskii, 1971a, 1971b), considering the widespread use of the term "tonstein" in the literature of the world, we suggest that coal partings of this type, altered by metagenesis or contact metamorphism, be called "meta-tonsteins," which has been used in several papers (Bouroz, 1962, and others).

The presence of heavy minerals in tonsteins has been noted by a number of investigators (Stach, 1950; Hoehne, 1954-1955; Stöffler et al., 1963; and others). Although they did not carry out special systematic studies, with rare exceptions (Stöffler et al., 1963), many authors have tried on the basis of determination of accessory minerals mainly in thin sections and polished sections to use them occasionally as a basis for attacking each other's point of view on the origin of tonsteins. The writer conducted such work first in the Donets Basin, although there had been a few references to the finding of rutile and quartz in thin sections of the kaolinite partings (Geological-Chemical Map of the Donets Basin, 1941), biotite, zircon, and a few grains of apatite (Brailovskaya, 1973). Preliminary results of the study of accessory minerals in 96 samples of tonsteins from 11 coal seams may be summarized as follows. Tonsteins from different coal seams were found to be quite simi-

lar in accessory mineral content. The heavy fraction (without iron sulfides and carbonates) amounts to only hundredths or tenths of a percent of the rock (limits established were 0.02 to 0.30%). No differences were noted in the vertical distribution of accessory minerals within the thin partings. Apparently no differentiation of the minerals by specific gravity took place either during sedimentation or during final settling out of the original material in the quiet, swampy waters. It is also characteristic that the overwhelming majority of accessory minerals are silt sized. Moreover, no difference in the size of these minerals was noted in samples from individual kaolinite partings taken over considerable areas. Consequently, it is also impossible to suggest mechanical differentiation of the material during transportation to the depositional site, just as it is impossible to establish any probable direction of supply of the original material of the tonsteins. Data presented on the size of the accessory minerals, especially on their lateral and vertical distribution in kaolinite partings, indicate that water currents can be excluded as an agent of transportation of the original material. However, these features do not rule out eolian transportation, which also accords well with the thinness of the partings combined with their exceptionally widespread distribution (many thousands of square kilometers).

The following minerals have been described among the accessories: zircon, apatite, rutile, garnet, tourmaline, corundum, and anatase. The most abundant accessories are apatite and zircon (generally more than 90-95% of the heavy fraction). Apatite predominates in most of the tonsteins studied (coal seams h_{11} , k_s^1 , k_s^2 , k_s^N , l_1 , l_3 , l_{e1} , m_3) while zircon does in tonsteins from k_s^V and m_3 . The ratio between apatite and zircon generally varies over the area of occurrence of individual kaolinite partings. Thus, tonsteins are distinguished from ordinary terrigenous coal-bearing rocks of the Carboniferous not only by a limited set of accessory minerals, but also by the fact that they are not "counted" with terrigenous mineral provinces established for such minerals (Logvinenko, 1973). Tonsteins are "transgressively" superimposed, as it were, on the terrigenous mineral provinces of the coal basin. This circumstance once again underscores their unique nature both in the relationships of the original material and in the conditions of transportation and deposition. Not to answer the question of the origin of tonsteins at this stage of the study of their accessory minerals, the writer notes that in heavy mineral content the tonsteins are quite close to kaolinite of the weathering zone of, e.g., granitoid rocks of the Ukrainian crystalline complex, where it is no more than 0.1-0.2% (Kramarenko, 1968), and which are also similar in the limited accessory mineral association (Rus'ko, 1974). It is therefore impossible to rule out that the oligomictic character of the tonsteins is a consequence of alteration of their original material, mainly in the area of dispersal and to a lesser extent during transportation, sedimentation, and subsequent burial in the peat bog. It is hardly possible to explain such a poor accessory mineral assemblage and the absence of poorly stable minerals in them only by the retention of tonstein material in the acidic environment of the peat bog, since in coal partings of other types and in the coal itself certain poorly stable minerals are preserved (Larishchev and Kurbatova, 1955).

Besides Ti, Mn, and P, noted in the chemical analysis, the presence of Zr, Ba, Sr, Ni, Co, V, Be, Cu, Ga, Pb, Zn, Cr, Se, La, and Y has been established in the kaolinite partings by spectroscopy. The difference between partings from different coal beds in the assemblage and amount of minor elements is generally small, whereas they are considerably poorer in these elements than the usual rocks of the overlying beds and soil of the coal seams or coal partings of other types. Such a paucity of minor elements in tonsteins may be explained by their monomineralic composition and the poor capacity for sorption of rock-forming kaolinite. The acid environment of the peat bog in which the deposition and alteration of the tonstein material took place also promoted more rapid desorption than retention of minor elements. Moreover it has to be noted that even when tonsteins are in direct contact with the overlying rock, soil, or parting composed of ordinary argillite or siltstone, i.e., occur in an environment identical with that of these rocks, they differ substantially in content and composition of minor elements. Everything, including the information cited above, suggests an undoubtedly different original material for these atypical coal partings, and possibly a difference in degree of alteration of the original material up to its deposition and burial in the peat bog as well.

The attempt to study the tonsteins of the Donets Basin indicates that the sum of the macroscopic features seen (color on a fresh surface, hardness, nature of the contacts and bonding with the coal, the presence of concretionary or other inclusions, position within the coal bed, and others) are so characteristic of each of the kaolinite partings described that in many cases they can be identified without using the microscope or other laboratory

tests. However, if these visually observed signs in the tonsteins vary, sometimes over small distances, then their specific petrographic traits and features of their chemical and mineralogical composition, determined by laboratory investigation, are characterized by amazing persistence and hold up with great success. This makes it possible to differentiate kaolinite partings accurately not only from other partings and coals, but also from one another. Patterns of lateral changes in the chemical and mineralogical composition of tonsteins, caused by the unequal effects of catagenesis and metagenesis in different parts of the basin, can be established and taken into consideration in identification of the coal seams containing the tonsteins.

And since kaolinite coal partings (or metatonsteins), persistent over wide areas and having unique traits and features, are found in a relatively small number of coal beds in the basin, the very fact of the presence of this parting in a coal bed is an important correlation index, turning the coal bed containing it into an index horizon of paramount importance. The writer has set for the basis for the possible use of kaolinite partings for the synonymy of coal beds and correlations of coal-bearing deposits, and for useful recommendations, in special papers on the subject (Zaritskii, 1971a, 1971b).

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THE USE OF DATA ON COMPOSITION AND HOMOGENIZATION TEMPERATURE
OF MICROINCLUSIONS IN SALT CRYSTALS IN SOLVING PROBLEMS OF GENESIS

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UDC 548.52

In his article "Conditions of formation of the Upper Vorotyshchenskii sediments of the Stebnik region," in: The Geology and Geochemistry of Combustible Minerals [in Russian], Vol. 44 (1975), V. M. Kovalevich describes the results of determinations of the chemical composition of single phase (liquid) and two phase (liquid + gas, or liquid + trapped crystallite) fluid inclusions, and the temperatures of homogenization of two-phase inclusions in various morphologic forms of halite, and draws conclusions on the conditions of formation of the Upper Vorotyshchenskii deposits around Stebnik. This is the first time that data on the composition and homogenization temperature of liquid and gas microinclusions in various morphologic forms of halite have been obtained from the Stebnik deposit, and the data may obviously be used to quantify the physicochemical parameters of the medium from which the minerals, containing the microinclusions, crystallized. Serious consideration must be given to the conclusions drawn regarding the conditions of formation of the halite layer.

The microinclusion parameters themselves (composition and homogenization temperature) obviously do not indicate the dependence of microinclusions and host minerals on a particular stage of lithogenesis (Kalyuzhnyi, 1960). Since compositionally similar varieties of the same mineral can form during various stages of the sedimentary process, during early and late diagenesis, katagenesis, and even hypergenesis, then microinclusions in genetically different mineral generations, if they really do reflect these different generations, will be characteristic of the different conditions. In order that concrete microinclusion parameters gain significance as indicators of conditions prevailing at particular stages of lithogenesis, it is necessary to know the exact, genetically diagnostic features of the mineral forms (the host crystals) containing the inclusions, independent of the method of study of the microinclusions. For example, in order to determine the geological conditions that characterize microinclusions of calcium chloride brine in halite crystals, it is necessary first of all to explain under what concrete conditions, and at what stage of lithogenesis, the host crystals formed.

The elucidation of the genetic nature of mineral species depends on the competence of the structural and textural petrographic analysis. Genetic mineral species deduced by this method serve as genetic "bench marks," relative to which it is possible to refer data on the composition and homogenization temperature of liquid and gas-liquid microinclusions to the same stage of lithogenesis as the surrounding crystal. If this condition is not fulfilled, it is meaningless to attempt to give a genetic interpretation to microinclusion data.

Unfortunately, it must be stated that, through familiarity with the work on microinclusions, microcomponents, and trace elements in halite and other salt minerals (Bilonizhka, 1970; Malikova, 1967; Petrichenko, 1973; Petrichenko et al., 1975), the role and significance of microinclusion study methods are exaggerated: the ability to solve genetic problems is ascribed to these methods, which do not embrace the problems. At the same time, the principal conditions — the immediacy and independence of determining the genetic affiliation of the mineral species, which contain the microinclusions, are either completely overlooked by the research worker concerned, or the problems are dealt with superficially, without taking account of their complexity or specific nature.

Kovalevich divides all the halite in the deposit into primary (sedimentary) and secondary (recrystallized). The subdivision of salt minerals, including halite, in Carpathian deposits into primary and secondary, sedimentary and recrystallized, is incorrect on objective grounds, and does not correspond with modern views of lithology in general, nor with

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Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 140-143, November-December, 1977. Original article submitted December 28, 1976.

the level of study of the lithology of Carpathian deposits in particular. The concepts "primary" and "secondary" are not equivalent in the amount of information they convey. "Primary" is synonymous with "sedimentary," and sufficiently precisely defines the initial, or primary, stage of lithogenesis. "Secondary" on the other hand, is a broad concept, that refers to the process of all subsequent stages of lithogenesis, including hypergenesis. In using such a subdivision, certain categories have to be compared, which are incomparable in a genetic sense.

The same applies to the concepts "secondary," and "recrystallized." Neither of these terms expresses anything concrete with respect to genesis. Recrystallization processes can and do continue at any time, and at any stage in the formation or destruction of rocks under corresponding conditions, and consequently are specifically genetic phenomena. For this reason, the above-mentioned subdivision has no sense from a classification point of view. The subdivision is also meaningless in a genetic sense since it is based on an outdated notion of the sedimentary (primary) nature of the potash rocks of the Carpathian deposits, including Stebnik, in which their formation was considered to have taken place under constant geochemical conditions, in a saline basin environment. It has not been shown (Khod'kova, 1964, 1971, 1973; Khod'kov and Khod'kova, 1966) that the rocks of the Carpathian deposits formed under genetically complex conditions, covering several stages, the main ones being sedimentary-early diagenetic, late diagenetic, and katagenetic. Each stage of lithogenesis has its own corresponding composition, and association of salt minerals, and each mineral, formed at a particular stage, has its own forms, colors, and characteristic impurities.

In particular, three genetic varieties of halite were identified and described (Khod'kova, 1972, 1973). The first, sedimentary-early diagenetic variety, occurs as solitary crystals in saline muds and silts; in the form of rock salt layers with a greater or lesser admixture of clay or silt; and as microinclusions in crystals and layer fragments of nonrecrystallized, glassy langbeinite. The second, late diagenetic variety, which displays a fibrous habit, occurs in rocks in the form of short, variably thick, mainly vertically oriented, veins (joint infillings). The third, katagenetic variety, occurs as horizontal, layered halite formations, developed on bedding planes and as elongate joint infillings; their layered nature results from their being formed at the margins of sedimentary-early diagenetic layers.

Judging by their macroscopic features, the halite forms, described by Kovalevich as sedimentary layer formation, are layerlike halite veins, formed during katagenesis. The presence of zoned skeletal crystals in layerlike halite formations within massive, granular halite, is by no means a conclusive indication of their sedimentary origin. Zonally distributed microinclusions of brine and gas are present in crystal form, including halite, which are known to have appeared during post depositional phases. Fibrous, vein, and coarsely crystalline halite varieties, forming pocket accumulations, described by Kovalevich as being the recrystallization product of primary sedimentary halite, are actually superimposed forms, which crystallized from solutions that were circulating in rock joints, mostly oblique to the bedding. There are no photographs or diagrams in Kovalevich's paper from which one could determine the exact genetic affiliation of the separate forms of halite.

The experience of a long number of years of work on the Carpathian potash deposits has shown that in the absence of a generally accepted classification and nomenclature for potash rocks, and of a unanimity of views concerning their conditions of formation, and considering also their exceptionally variable composition and complex depositional conditions, verbal formulations of the geological associations and characteristic features of the specimens under investigation are quite insufficient. It is necessary to indicate on photographs and sketches at 1:50 and 1:1 scales of parts of outcrops, and mine walls from which the specimens were collected, the exact collecting point; the specimens themselves should also be illustrated, on a large scale. With exact visual documentation, it is possible to test the validity of a genetic diagnosis, and, where necessary, to refine and correct it.

This last remark applies to Kovalevich's understanding of the genetic significance of triangular diagrams. The location of solution points on particular parts of so-called marine diagrams in no way indicates that the solutions are marine. The diagram illustrated by the author characterizes equilibrium compositions of solid and liquid phases at a particular temperature and pressure in the system $\text{Na-K-Mg-Cl-SO}_4\text{-H}_2\text{O}$. The compositions corresponding to the points on the diagram could just as well represent evaporated ocean water, as an

underground solution in rocks, the minerals of which are composed of the elements indicated above.

From the above, only one conclusion may be drawn. Since Kovalevich has not demonstrated to which stage of lithogenesis the halite forms selected by him belong, data on composition and homogenization temperature of liquid and gas microinclusions cannot be used to draw conclusions of a genetic nature.

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TRIVALENT MANGANESE IN MINERALS

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UDC 549.521.61

In her works entitled "Chemical and mineralogic studies of manganese ores," and "Manganese valencies in minerals," Bazilevskaya (1976a, b) sharply criticizes some of my earlier publications on the valency states of manganese in natural oxides and hydroxides. I consider it my duty to continue the discussion of this problem, and to give a comprehensive reply to Bazilevskaya's critical remarks.

1. It is widely known that x-ray spectroscopy and a series of other physical methods, which allow a substance to be studied without destroying its crystal structure, give immediate information on the composition of a particular ion in a crystal.

Despite Bazilevskaya's opinion (1976b), the author does not claim priority in applying the x-ray method to the study of manganese oxide compounds, nor in modifying the method. Manganese valency states in synthetic compounds have previously been studied, using red spectral x-ray absorption, by Vainshtein et al. (1963), and Kirichok and Karal'nik (1967). Other examples of the use of x-ray spectroscopy in determining the valency of transition elements in compounds are known.

2. The application of the method for studying natural oxides and hydroxides of Mn requires primarily the careful selection of samples. The most important condition is for the analytic specimen to be monomineralic. This condition demands a reliable description and detailed study of the sample, for which a variety of analytic methods are available — x-ray, thermographic, chemical, and spectral. Since heating any oxide of manganese (in vacuo or in air) to a particular temperature results in characteristic phase changes or chemical reactions for each oxide, x-ray analyses were done on the thermal alteration products of each sample.

In order to prevent oxidation, grinding, mixing, and preservation of specimens was carried out in acetone or alcohol. Synthetic mixtures of manganosite-pyrolusite and pyrolusite-manganite were similarly treated. It should be noted that since the energy level and the nature of the fine red field absorption structure are determined by the atomic-absorption field, and by the parameters of the nearest atomic coordination, it is quite in order to use a mechanical mixture as a standard for mixed valency manganese oxide. Preparation of samples for red spectral absorption photography was made in a celluloid solution. The use of this material as a bonding agent prevents oxidation of samples, and makes them suitable for prolonged preservation.

Natural and synthetic mineral samples, with known structures, were used as standards; these were manganosite, hausmannite, bixbyite, manganite, pyrolusite, and ramsdellite.

Manganosite. Obtained on heating Mn_2O_3 for 4 h at 800°C in vacuo. The sample was a gray-green, finely crystalline mass. A method for synthesizing manganous oxide has been described by Rode (1952).

The x-ray photograph of the specimen used corresponds to that for manganosite (ASTM, 7-230). The primitive cell parameter is $a = 4.449 \pm 0.003 \text{ \AA}$. The DTA curve is similar to the thermogram of "inactive" MnO , presented by Rode (1952).

Hausmannite. Two specimens of this mineral were used as standards. A specimen from Nordmarken (Norway) was a brownish-black, finely crystalline aggregate, with a submetallic luster, in association with quartz. The primitive cell parameters are $a = 5.76$, $c = 9.44 (\pm 0.01) \text{ \AA}$.

Of the minerals capable of replacing Mn, Zn ($\approx 1\%$), and Fe (0.1%) were found in the x-ray analysis of this specimen.

Ivan Franko State University, Lvov. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 144-149, November-December, 1977. Original article submitted February 25, 1977.

Synthetic hausmannite, a brown powder, was obtained on heating for 1 h in air at 1000°C, a finely ground sample of pyrolusite from Horná Platna (Czechoslovakia).^{*} The primitive cell parameters are $a = 5.76$, $c = 9.46 (\pm 0.01)$ Å. No thermal effects were noticed on the thermograms of hausmannite which had been heated to 1000°C.

Hausmannite, $Mn^{2+}Mn_2^{3+}O_4$, and hetaerolite, $ZnMn_2^{3+}O_4$, belong to the tetragonally distorted type of spinel, with the c/a ratio of the primitive cell parameters being ≈ 1.6 .

From a study of $ZnMn_2O_4$ - $ZnFe_2O_4$ solid solutions, it has been shown that the c/a ratio decreases as the Fe^{3+} content increases (Romeijn, 1953). The Fe^{3+} ion, it should be noted, can replace neither Mn^{2+} nor Mn^{4+} . This fact excludes a hausmannite formula of the form $MnO \cdot MnO \cdot MnO_2$, which appears in Bazilevskaya's work (1976a).

Bixsbyite. It has been shown by Morozov and Kuznetsov (1950), Rode (1952), and Kulp and Perfetti (1950) that β and γ modifications of MnO_2 are altered to a cubic modification of Mn_2O_3 , on being heated in air in the temperature range 550-700°C. This method has been used to obtain synthetic bixsbyite. With regard to Bazilevskaya's remarks that Mn_3O_4 , not Mn_2O_3 , results from heating pyrolusite to 720°C, the following quotation is relevant (Bazilevskaya, 1976a, p. 38): "The first endothermic effect on heating pyrolusite usually takes place at 640-680°C, and results in β - MnO_2 changing to β - Mn_2O_3 ."

A black powdery form of Mn_2O_3 was obtained on heating in air a crushed sample of pyrolusite from Horná Platna. The x-ray photograph corresponded to that for cubic Mn_2O_3 (ASTM, 2-0896), with $a = 9.409 \pm 0.005$ Å.

Bazilevskaya (1976a, p. 16) reproaches me for the fact that "the valency state of manganese ions in this oxide, as well as in manganite, has not been firmly established." Experimental studies of phase diagrams for the Mn_2O_3 - Fe_2O_3 system (Toropov et al., 1969) make discussions on the subject of the valency of manganese in Mn_2O_3 superfluous. Natural bixsbyite $(Mn, Fe)_2O_3$ shows a perfect resemblance to the trivalent manganese standard, irrespective of how much isomorphous Fe^{3+} is present.

Manganite. A study has been made of manganite specimens of hydrothermal and sedimentary origin. The characteristic features of the samples and results of their detailed study have been published previously (Fenoshina and Yanchuk, 1974). Well-crystallized hydrothermal manganite samples from the Dzhezdy (Kazakhstan) and Ilfeld (Hartz Mts., GDR) were used as standards. The primitive cell parameters of the Dzhezdy manganite are $a = 8.92$, $b = 5.27$, $c = 5.74$ Å, and for the Ilfeld material $a = 8.91$, $b = 5.27$, $c = 5.74 (\pm 0.01)$ Å (using ASTM, 8-99, $a = 8.91$, $b = 5.28$, $c = 5.74$ Å).

Concerning the valency state of Mn in manganite, Bazilevskaya (1976a, p. 89) notes: "An analysis of published data, as well as my own experiment, suggests the presence of Mn ions of mixed valency in manganite, not manganese trioxide, which the majority of mineralogic reference books take to be the case." On what actual data are most of these reference books based? Bazilevskaya casts doubt on all experimental data concerning the presence of trivalent manganese in manganite, while data on divalent and quadrivalent Mn in manganite are considered "objective experimental studies."

Ignorance of structural studies permits Bazilevskaya to maintain that manganite has a molecule of water of crystallization (but not the OH^- group), as shown by Dach's (1963) neutron diffraction studies, and has the formula $MnO \cdot MnO_2 \cdot H_2O$.

Neither is it clear how the results of investigating perovskite-type compounds $[(1-x)La, xCa] \cdot MnO_3$ (Wollan and Koehler, 1955) can indicate, according to Bazilevskaya, various valency states of Mn in manganite. Moreover, the authors note that these compounds correspond to the ideal formula ABO_3 , where A represents large ions of La^{3+} , Nd^{3+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , etc. and B = small ions of Mn^{3+} , Co^{3+} , Ti^{4+} , Mn^{4+} , etc.

The x-ray and IR spectroscopy methods (Yanchuk, 1969; Boldyrev et al., 1971) have established trivalent manganese in manganite, which is supported by the formula of this mineral, $MnOOH$.

It is widely known that in the manganese dioxide minerals, pyrolusite and ramsdellite, manganese ions occur in the quadrivalent state.

^{*}The spectral analysis results from the Horná Platna pyrolusite sample show it to be practically free of impurities. For this reason, it has been used in the synthetic production of hausmannite and bixsbyite.

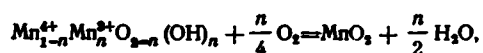
Bazilevskaya (1976b, p. 147) maintains that "there have been no problems in the mineralogy of manganese in pyrolusite up to now" (i.e., up until my work — E. Ya. Yanchuk). However, a significant number of workers (Feitknecht et al., 1960; Fleischer et al., 1962; Perederiev, 1956; Rode, 1952, et al.) have shown that dioxide compositions do not correspond fully with the ideal formula, the O:Mn ratio being less than 2, as a result of the presence of a small amount of low-valency Mn ions.

The use of pyrolusite and ramsdellite as standards for quadrivalent manganese in x-ray spectroscopy has necessitated the careful study of these minerals (Yanchuk and Mel'nikov, 1972). A small exothermic effect appears on pyrolusite and ramsdellite thermograms in the 200–250°C temperature range. On the ramsdellite thermogram, this effect is known to occur before the exothermic effect corresponding to the γ -MnO₂– β -MnO₂ polymorph transition. The x-ray studies have shown that tempering ramsdellite at the temperature of this exothermic effect (but no higher) does not result in its being transformed to pyrolusite.

On the basis of x-ray studies of the valency state of manganese in initial and tempered specimens of pyrolusite and ramsdellite, it is concluded that insignificant quantities of trivalent Mn are present in initial samples, as well as quadrivalent ions.

The problem of compensating the negative charge in the pyrolusite and ramsdellite structure, due to the presence of Mn³⁺ ions, can be solved by determining the amount of water in the specimens: This is done by measuring the loss of weight on heating. An insignificant weight loss is observed at the temperature of the exothermic effect. Two processes thus take place simultaneously: dehydration, accompanying the endothermic effect, and oxidation, accompanying the exothermic effect. Since the latter predominates, a low exothermal peak is found on pyrolusite and ramsdellite thermograms. A similar pattern also emerges in the case of manganite, where, however, a predominantly endothermic effect occurs on heating, related to the dehydration of manganite. Only partial oxidation takes place in this case. It may also be noted that, on examining the manganosite DTA curve, one can be convinced of the presence on the curve of a very strong exothermic effect, corresponding to the oxidation of MnO.

Removal of water at the temperature of the exothermic effect on the pyrolusite DTA curve shows a relationship between dehydration and oxidation of Mn³⁺ ions, which would be difficult to explain if water, in the form of the neutral H₂O molecule, were present, the expulsion of which could occur, unrelated to the oxidation of Mn³⁺, and would appear as an endothermic peak on thermograms. Thus, the following process occurs:



where $n = 0.03\text{--}0.07$ for the samples presently under discussion.

The standards used were well-crystallized pyrolusite from Horná Platna (Czechoslovakia) and Ilfeld (Hartz Mts., GDR), and ramsdellite from the Kochash Valley, Rhodope Mts (Bulgaria). Since Mn³⁺ ions are present in pyrolusite and ramsdellite, the standards were first tempered at the temperature of the above-mentioned exothermic effects, before the preparation of the synthetic mixtures and absorbents for x-ray absorption photography.

3. Bazilevskaya suggests that there is no basis for my doubting the valency of manganese in the so-called psilomelane-type group of minerals, with the general formula RO·MnO₂·nH₂O, "where R represents Mn²⁺, Ba, Ca, K, Pb, Cu, etc." (Bazilevskaya, 1976a, p. 15). It should be remembered that this "group" includes a whole series of separate mineral species, each with its own distinctive composition (which may be variable) and structure, and their formulas do not correspond at all closely with that shown above.

Structural studies (Byström and Byström, 1950; Wadsley, 1952) have shown that K⁺, Ba²⁺, and Pb²⁺ ions in minerals of the isomorphic series cryptomelane–hollandite–coronadite, and Ba²⁺ in romaneshite, occupy different structural sites from manganese. The todorokite and burnsite structures have not been studied. However, from crystal chemistry and conditions of formation, it may be assumed that Mg²⁺, Ca²⁺, Ba²⁺, Sr²⁺, Na⁺, and K⁺ ions in these minerals also occupy different sites from manganese ions. As a result of these ions entering into the structure of complex manganese oxides, Mn⁴⁺ ions have been partially replaced by manganese of lower valency (sorption of Mn²⁺ ions onto MnO₂ hydroxides apparently does not take place in this case). The latter occupy the same sites as Mn⁴⁺ ions, and create a corresponding compensation for the excess positive charge, as noted by Byström and Byström

(1950), and Wadsley (1952). The x-ray and IR spectroscopy methods on complex oxides and hydroxides have established the presence of trivalent manganese side by side with quadrivalent (Yanchuk and Povarennykh, 1976).

4. Bazilevskaya has accused me of drawing conclusions that contradict notions of the electron structure of the manganese atom, and the energy levels of transitions in the electron shells, while at the same time making use of certain notions which are not sufficiently well founded. As proof of the extremely widespread distribution of Mn^{2+} and Mn^{4+} ions in natural oxides and hydroxides, Bazilevskaya (1976a) uses the fact that d^5 and d^{10} electron configurations are the most stable. For this, she referred to the work of Shchukarev (1945), who examined the thermal stability of manganese and iron oxides, as if this proved that "di- and quadrivalent states of manganese were more advantageous in energy terms, compared with the trivalent state" (Bazilevskaya, 1976a, p. 16). How is it possible to reconcile these statements with the well-known fact that manganosite (a divalent manganese oxide) is unstable, and oxidizes readily in air? Shchukarev (1945) has noted that special conditions are necessary to produce a lack of balance in manganese oxides, particularly the action of acids.

As far as the energy advantage of the $Mn^{2+} \rightarrow Mn^{4+}$ oxidation process, compared to $Mn^{2+} \rightarrow Mn^{3+}$, is concerned, Bazilevskaya considers that proof is given by values of oxidation-reduction potentials, presented by Latimer (1954). The oxidation potential for the reaction $Mn^{2+} = Mn^{3+} + e^-$ is 1.51b, and for the reaction $Mn^{2+} + H_2O = MnO_2 + 4H + 2e^-$ is 1.23b. It should be pointed out that the oxidation-reduction potentials as quoted are measured for acid solutions. Referring to the potential of the system $Mn^{2+} \rightarrow Mn^{3+}$, Latimer notes: "For the potential of the system $Mn^{++} \rightarrow Mn^{+++}$, we use the value obtained by Grube and Metzger..., although the transition took place in concentrated sulfuric acid, and a significant correction is necessary, to take into account the activity coefficient, the value of which is unknown" (Latimer, 1954, p. 28).

Gorbachev and Shpital'skii (1940) have shown that reduction of Mn^{3+} to Mn^{2+} takes place in very concentrated H_2SO_4 (>15 N). This also evidently explains the energy disadvantage of the oxidation reaction $Mn^{2+} \rightarrow Mn^{3+}$.

The most stable valency form of manganese under exogenic conditions is quadrivalent manganese, with three 3d electrons.

5. My conclusions concerning the wide distribution of Mn^{3+} ions in manganese minerals, based on a study of the detailed structure of x-ray absorption spectra of manganese in oxides and hydroxides, have been confirmed by IR spectroscopy (Boldyrev et al., 1971; Yanchuk and Povarennykh, 1975a, b, 1976).

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In a recently published monograph, "Ferromanganese Concretions from the Pacific Ocean" (1976), the results of many years of research work on these extremely interesting bodies are presented. This splendidly produced book gives a very complete picture of modern views on ocean floor ore deposits. The usefulness of such a publication, and the great scientific interest in the problems raised, is indicated by the fact that the book has become a rarity, almost as soon as it reached the bookshops.

The various sections of the monograph are, unfortunately, not all equally valuable. The interpretation of data concerning the mineral composition of concretions, presented by P. F. Andrushchenko in Chap. 5, is open to criticism. Her attempt to develop ideas about particular features of the chemical composition and internal structure of basic ore forming minerals in concretions, on the basis of mineralogic studies, cannot be accepted as satisfactory. This can be demonstrated using todorokite, a sufficiently widespread mineral in concretions, the characteristic feature of which is the absence of a stoichiometric relationship. Different authors ascribe formulas to todorokite which vary slightly in the quantity and series of elements in manganese compounds.

Andrushchenko used a mineralogic method to separate a monomineralic todorokite fraction from closely intergrown todorokite and manganese hydroxide colloids in concretions. Crystallochemical formulas were obtained for two todorokite samples from the separates. The following formula was obtained for sample 6: $(\text{Mg}_{0.83}\text{Na}_{0.53}\text{K}_{0.20}\text{Mn}^{2+}_{0.18}\text{Al}_{0.13}\text{Ba}_{0.02})_2\text{Mn}^{4+}_{0.11.7}\cdot 3\text{H}_2\text{O}$, while sample 7, monomineralic todorokite with a radial structure, gave $(\text{Mn}^{2+}_{0.82}\text{Ca}_{0.74}\text{Mg}_{0.27}\text{Na}_{0.12}\text{K}_{0.03}\text{Ba}_{0.02}\text{Mn}^{4+}_{0.11.93}\cdot 3\text{H}_2\text{O})$.

The method of calculating oxygen raises certain doubts, since it is clear from subsequent statements that the author accepts the well-known viewpoint of Buser and Grütter (1956) on the presence in the todorokite structure of alternating layers of MnO_2 and $\text{Mn}(\text{OH})_2$. These formulas are interpreted as follows: "The slight shortfall in oxygen ions in the calculated formulas (11.7 and 11.93, as against 12) is probably caused by the presence of OH^- in the mineral, which is the same size as the oxygen ion. The chemical data used in calculating the crystallochemical formula of todorokite also display a certain surplus of MnO_2 and H_2O , resulting from the presence of an insignificant amount of vernadite as an impurity in the sample" (op. cit., pp. 136-137 (1976), my italics — E. B.). Two mutually exclusive positions occur together — a shortfall in oxygen ions cannot be accompanied by a surplus of MnO_2 , since in reality these are one and the same thing, as MnO_2 is determined from oxygen activity. The lack of oxygen ions in manganese ore analyses is used to determine Mn^{2+} . This value appears in the formulas, hence the observations as presented are unintelligible.

Moreover, in calculating the above formulas, nearly all chemically determined oxides were used, since the author excludes these from notions about the monomineralic composition of the samples. However, the following remarks are made later: "The calculation of the mineralogic composition of sample 6, using chemical and x-ray data, and microscope observations, shows that todorokite amounts to about 84%, pyrolusite 2.8%, vernadite 3.8%, quartz 9.4%; while sample 7 yields todorokite 84%, pyrolusite 5%, vernadite 4%, and impurities 7%" (op. cit., p. 137). The calculated formulas therefore represent a mixture of minerals, not pure todorokite. It is also unclear how there could be 9.4% quartz in sample 6, if the chemical analysis gave a total of 1.67% SiO_2 . Impurities in sample 7 amount to 7% from a modal analysis, while from the chemical analysis, this value can be at most 0.52%, which is the remainder in the crystallochemical formula, left by excluding the oxides SiO_2 , CO_2 , and Fe_2O_3 . Chemical data should not be distrusted, since petrographic studies of weakly recrystallized

Institute of Geology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 149-152, November-December, 1977. Original article submitted December 20, 1976.

and amorphous manganese oxide minerals are more subjective. This is also confirmed by data from x-ray and thermal studies.

A strong reflection at 7.02-7.18 Å in the todorokite sample under investigation is indicative of another mineral, bernessite, which is found distributed throughout concretions. Marked reflections at 2.44 Å and 1.41 Å also confirm the presence of this mineral.

One cannot agree with the interpretation of the results of thermal studies done on these samples. Using the chemical data, it is possible to calculate the weight loss for various temperature intervals. The calculations do not correspond with Andrushchenko's views on the loss of various types of water up to 500°C, and the todorokite-hausmannite transformation at 650°C. Weight loss curves, illustrated in the article, indicate a higher temperature for this transformation, around 900°C. There is no correspondence either with the total weight loss, which, according to the derivation diagram, is 19.7% and 19.1% for samples 6 and 7, respectively, while the chemical data in both cases indicate a value of not less than 22%. One must suppose, therefore, that the author was unable, with the aid of a microscope, to select identical samples for different types of analysis, so that noncomparable results were obtained.

We will not dwell so scrupulously on other manganese minerals, identified in concretions, except to point out that, in overestimating the possibilities of the petrographic method, the author has not paid sufficient attention to the data from other research methods. The identification of a large number of minerals does not reflect the true composition of the most widely distributed ferromanganese concretions. In places, this becomes an end in itself, and the author, in studying an extremely rare type of hydrothermally altered concretion, has notably supplemented the list of known minerals in concretions. This was done basically by using a combination of petrographic and x-ray techniques. However, the possibility of separating pure minerals from concretions is very limited, as indicated by the todorokite example cited above, hence x-ray data alone are insufficient for obtaining the composition of the pure form of any particular mineral.

For example, brownite has been identified for the first time in hydrothermally altered concretions, simultaneously with todorokite, pyrolusite, vernadite, etc. Such a mineral association is difficult to explain. Brownite is a high-temperature, anhydrous silicate, which forms whenever other manganese hydroxides cannot survive.

In conclusion, the work does not clarify the expediency of singling out vernadite as a basic ore-forming mineral in concretions, since the x-ray peaks at 1.40 Å and 2.40 Å, which are ascribed to vernadite, are typical of δ -MnO₂, which is natural bernessite. This introduces confusion into the nomenclature of manganese minerals in concretions, and leads the author to great uncertainty in identifying bernessite, a universally recognized mineral in concretion mineralogy. One cannot agree with the assertion that it is possible to confuse bernessite with kaolinite, or with several zeolites that have similar x-ray peaks. In any case, the article is about a manganese mineral, known in nature, and quite definitely isolated from a synthetic phase. Judging solely by individual x-ray peaks, it is possible to find nearly all characteristic lines for a particular mineral, which other workers have illustrated in reference manuals.

The mineral composition of ferromanganese concretions has been repeatedly discussed in the works of foreign researchers, and, although there are a few differences of interpretation in some questions, all the authors, Andrushchenko included, quote the work of Buser and Grütter (1956). As a result, the basis for calculating crystallochemical formulas of manganese minerals in concretions should be manganese dioxide, which makes it impossible to introduce labeled indicators of the degree of oxidation of manganese in these formulas. Changes in this method of calculation can only be done on the basis of specialist studies, which Andrushchenko has not carried out. The optical method of studying polished sections in reflected light is, firstly, somewhat subjective in the case of intergrowths of minerals that are finely dispersed and amorphous to x rays, and, secondly, does not reveal the crystallochemical nature of these minerals.

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TEN YEARS OF WORK OF THE SIBERIAN SECTION OF THE INTERDISCIPLINARY LITHOLOGIC COMMITTEE

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UDC 55(091)

In May 1965 the Commission on Sedimentary Rocks of the Earth Sciences Section of the Academy of Sciences of the USSR, reconstituted at the end of 1974 into the Interdisciplinary Lithologic Committee, passed a resolution to found a Siberian Branch, and decided its composition.

From its inception, the Siberian Branch had as its aim the discussion of broad problems in various branches of lithology, geochemistry, paleogeography, sedimentary ore genesis, and oil and gas reserves of Siberia and the Far East. Decisions made during the course of these discussions were communicated to all scientific and industrial organizations carrying out similar work. Conference papers and reports have been published systematically in *Litologiya i Poleznye Iskopaemye*, *Geologiya i Geofizika*, *SNIIGGIMS Proceedings*, etc. Conference themes considered a wide range of problems in theoretic, applied, and regional plans.

The first conference (Novosibirsk, 1966) dealt with the theoretical basis of the lithoformation method developed by a group of Siberian lithologists. The method allows geologists to fix the major periodicity of sedimentation, controlled by alternations of different geotectonic regimes. It is based mainly on a subdivision into epochs of intense chemical weathering, for which a series of practical methods have been developed. To a certain extent, the meeting gave the reaction of Siberian lithologists to criticisms of the method, which had been voiced at a special seminar of the Commission on sedimentary rocks in 1964.

The following three conferences had an applied aspect and were devoted to problems of bauxites (II, Krasnoyarsk, 1967), phosphorites (III, Novokuznetsk, 1967), and lithogeochemical features of oil- and gas-bearing rocks of Siberia and the Far East (IV, Tyumen, 1968).

The examination of a wide variety of questions concerning the development of bauxite exploration in Siberia demonstrated the necessity of carrying out a sufficiently large volume of scientific studies concerned with establishing in sections those horizons that formed during epochs of intense chemical weathering on continents, the study of substrate rock composition, paleogeographic, paleotectonic, and geomorphologic reconstructions, and, as a result, obtaining the basis of the bauxite potential of individual regions.

The Siberian and Far Eastern phosphorite research program, selected as the subject for the third conference, considered the solution of problems of a genetic nature, the determination of patterns controlling the location of phosphorites in space and time, the lithogeochemical study of phosphorite bearing formations, technological studies of different ore types, etc. It was decided that the production of a map of phosphorite-bearing formations in the Altai-Sayan and Baikal fold zones, on a scale of 1:1,000,000 was necessary. The map was compiled under the leadership of V. P. Kazarinov and N. A. Krasil'nikova; a large number of authors cooperated on the project, and the map was published in 1970. In 1972 the monograph "Phosphorite Formations of Southern Siberia" (Krasnoyarsk Izdatel'stvo) was published, which formed an extended explanatory essay on this map.

The fourth conference, "Lithology and geochemistry of oil- and gas-bearing rocks of Siberia and the Far East," recommended, on the basis of various lines of research that had been pursued, that there should be a marked increase in the study of the composition and structure of productive beds, in order to explain the degree of inhomogeneity; to uncover any general pattern of changes in the reservoir and screening properties of the rocks, dependent on conditions of deposition and processes of secondary alteration; to reveal the distinguishing features of oil-, gas-, and water-bearing reservoir rocks; to develop an exploration method for lithologically screened oil and gas deposits; to pursue research in the field of epigenesis, and in detailed quantitative substage analysis; and to study factors

Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 153-155, November-December, 1977.

controlling the accumulation and alteration during diagenesis and katagenesis of dispersed organic matter in terrigenous, carbonate, and carbonate-halogenous rocks. Attention was drawn to the need for developing work on the reconstruction of paleolandscapes in the past, and in compiling geochemical maps, and maps showing content of organic matter and bitumens, as well as other research.

The fifth conference (Irkutsk, 1969) looked at a wide range of questions concerning lithogenesis and ore genesis of the Siberian Platform. The ninth conference (Novosibirsk, 1973) was also of a regional nature and was devoted to lithology and sedimentary mineral deposits of the West Siberian Platform. The conferences initiated a research program of these major regions of the Soviet Union.

The theme of the sixth conference (Krasnoyarsk, 1970) was the distribution in time and space, in Siberia and the Far East, of continental sedimentary breaks and weathering shells, related to the investigation of bauxite problems. Approval was given to the setting up of an interdisciplinary editorial committee to produce an annually revised map of Siberian bauxite potential at a scale of 1:2,500,000.

Maps and explanatory descriptions were published in 1970 and 1972 under the editorship of V. I. Bgatov and V. P. Kazarinov. A variation of the map, supplemented by new information for the entire territory of Siberia and the Far East, has now been prepared for publication. During a series of sessions devoted to solving problems of bauxite exploration, it was acknowledged that attention would need to be given to the extremely insufficient level of study of weathering shells and continental breaks in Siberia and the Far East; to the lack of information on the material composition of a series of weathering shell formations; and to the highly contradictory opinions on the age of weathering epochs.

Theoretical aspects of correlating sections of sedimentary rocks using lithogeochemical indicators formed the subject of the seventh conference (Tomsk, 1971), which noted widespread changes in the practical use of this method in Siberian geology. A series of contributions set out the results of inter- and intraregional correlation of rocks of various ages, based on methods of lithoformation analysis, and, in particular, the comparison of horizons of highly mature rocks. The conference program included communications on the results of work on coordinating sections based on petrographic, mineralogic, and geochemical analyses, as well as examples of correlation by means of horizons containing ash material and concretions, textural features of sediments (slump structure, in particular), facies rhythms, and other indicators. The possibility was shown of comparing sections in different regions by using the degree of development of bauxites, phosphorites, iron ores, and other sedimentary mineral resources.

Various problems in Precambrian lithogenesis and ore genesis were examined at the eighth conference (Khabarovsk, 1972), which dealt with applied aspects and scientific methodology. The importance of the problems that were discussed results from the fact that in Siberia and the Far East, the Precambrian is still the least-studied part of earth history. Also, related to Precambrian formations are the largest deposits in the world of iron-manganese ores, highly aluminous rocks, phosphorites, graphites, uranium, gold, polymetallic ores, and other minerals. In the Upper Riphean and Vendian of Siberia and the Far East there are ferruginous quartzites and manganese ores, and oil and gas accumulations. The Boksonskii bauxite deposit and a series of ore shows are associated with these sediments. Phosphorites, vanadium-bearing phanites, and ore shows of nonferrous and rare metals are found in several regions. An analysis of the available material allows one to identify in Precambrian history several major episodes of exogenic ore formation, traceable on all continents, and reflected in the structure of comparable sections in Siberia and the Far East. Upper Riphean, Vendian, and basal Cambrian sediments formed during a single ore epoch received particular attention during the course of the conference.

The tenth conference (Ulan Ude, 1974) dealt with the problems of stages of lithogenesis and patterns of sedimentary mineral deposit localization in Siberia and the Far East, while the eleventh conference (Irkutsk, 1975) considered different aspects of continental lithogenesis and the nature of weathering shells in the same region.

During the tenth conference attention was paid to the fact that in many geologic organizations in Siberia and the Far East, the collection of factual material was actually going ahead faster than the data could be systematized and generalized, and any generalizations made did not, as a rule, extend beyond the limits of comparatively small areas. The pro-

gram adopted by the conference was to provide for the compilation of maps showing reserves, economic geological analyses, and the establishment of basic patterns of occurrence in Siberia and the Far East of bauxites, agricultural minerals, ferrous and nonferrous metals, gold, building materials, and other types of sedimentary mineral raw materials. Special attention was paid to the necessity of making a rapid evaluation of the sedimentary mineral perspective of regions adjacent to the Baikal-Amur railroad tracks.

The program adopted at the eleventh conference considered the further development of research on the material composition of weathering shells and related mineral resources; obtaining a more refined and exact age for the formation of such shells; an assessment of the influence of the rock substratum on the weathering products; as well as a series of related studies of other problems in continental lithogenesis and ore genesis.

In addition, three methodology seminars were held during this period, at Novosibirsk, in 1962, 1973, and 1975.

What has been presented above shows that the Siberian Branch of the Interdisciplinary Lithologic Committee has systematically arranged the broad coordination of lithologic research, paying particular attention to the mineral raw materials of Siberia and the Far East.

The 1976-1980 program of work for the Siberian Branch was adopted at the tenth conference. The following conferences were proposed.

XIII. "Geology of the Aluminium Resources of Siberia and the Far East," and a seminar on exploration methods and diagnostic features of aluminohydrocarbonates (1977, Khabarovsk).

XIV. "Geology of the Phosphate Resources of Siberia and the Far East" (1978, Chita).

XV. "Problems of Oil- and Gas-Bearing Properties of the Siberian Platform," and a seminar on oil and gas traps (1979, Irkutsk).

XVI. "Problems of Sedimentary Ores of the Siberian Platform" (1980, Krasnoyarsk).

XVII. "Lithogenesis of Volcanosedimentary Rocks of Siberia and the Far East" (1981, Petropavlovsk-Kamchatskii).

At the present time, the Siberian Branch of the Interdisciplinary Lithologic Committee has 48 members, representing the regional geological surveys of Siberia and the Far East, as well as most of the scientific-research institutes and higher education establishments working in this territory. The executive committee of the branch comprises the following members: V. P. Kazarinov (president), V. I. Bgatov (vice-president), R. G. Matukhin (vice-president), T. A. Divina (scientific secretary), T. I. Gurova, Yu. P. Kazanskii, A. S. Kalugin, A. E. Kontorovich, and Z. Ya. Serdyuk.



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